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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

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A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Lieut. S. E. Blackstone is returning home from Venezuela.
Mr. K. A. Campbell is home from California.
Mr. A. P. Catherall is returning to Trinidad.
Mr. J. L. Harris is home from Trinidad.
Mr. G. Hunter has returned from India.
Mr. G. W. Lepper is returning to Burma.
Mr. F. A. Marr has left for Assam.
Mr. P. Meyer is home from Trinidad.
Mr. H. F. W. Morris has returned from India.
Mr. R. Nisbet is in Burma.
Mr. P. N. D. Porter is home from Singapore.
Mr. A. H. K. Radjy is in Persia.
Mr. J. W. Reid has returned to Persia.
Mr. S. Taylor Rogers has left for Ecuador.
Mr. L. S. B. Simeon is in Japan.
Mr. F. S. Smith has returned to Mexico.
Mr. D. A. Sutherland has returned home from the Near East.
Mr. C. Thomas has returned to Assam.
Mr. J. Westbury is returning to Trinidad.

The Secretary would be glad to learn of the whereabouts of the following members: E. E. G. Agius, A. E. Corbet, E. J. S. Hewitt, J. Jawad Jafar, A. MacLean, D. J. Pull, P. A. Stiff, P. A. Stiff, R. W. Stiles and E. Stokoe.

BACK NUMBERS OF THE JOURNAL.

The Institution is desirous of purchasing a limited number of clean copies of Journal No. 35, February, 1923, and of Journal No. 67, April, 1928. The price which will be paid for such copies is 7s. 6d., and all inquiries should be sent to the Secretary.

ROYAL AËRONAUTICAL SOCIETY.

At the meeting of the Royal Aëronautical Society, to be held on January 18th, 1934, at 6.30 p.m. at the Royal Society of Arts, John Street, Adelphi, London, a paper on "Ethyl" will be read by Mr. F. R. Banks.

The Council of the Royal Aëronautical Society have extended a cordial invitation to members of the Institution of Petroleum Technologists to attend the meeting and take part in the discussion.

CORRESPONDENCE.

Although the columns of the Journal of the Institution are open for correspondence, comparatively little use has been made of this facility in the past. The Council feel that more extensive use might be made of this by members who wish to record briefly matters of interest, experiences with regard to technical problems or difficulties, or to obtain information on some particular technical subject. In this way home and foreign members would be kept more in touch with each other and with technical matters of current interest, and it is hoped that a more general use will be made of the Journal.

SMOKE POINT OF KEROSINE.

Details of the standard method for the determination of the Smoke Point of Kerosine (I.P.T. Serial Designation K. 36) are now available in pamphlet form, and can be obtained from the offices of the Institution, price 6d. each.

No. 120. Vol. 19.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

A Theoretical Comparison of Petroleum Distillation Systems.

By PERCY MEYER, B.Sc., F.I.C.*

A relative knowledge of the degree of fractionation effected by batch or continuous distillation systems, with varying reflux ratios and number of bubble-plates, is desirable for many purposes.

In this paper the degree of separation obtainable by distilling a 0°–400° C. straight-line boiling mixture into 50 per cent. overhead and 50 per cent. residue, is calculated. Published results on equilibrium flash vaporisation provide an experimental check on the method of calculation used.

The feasibility of comparing the relative efficiencies of various distillation systems by means of an "overlap coefficient" is discussed.

Nomenclature.

y = mol. fraction lighter component in vapour.
x = mol. fraction lighter component in liquid.
K = volatility ratio.
= ratio of the vapour pressures of the pure components of a binary system.
T = mean temperature of distillation system (°C. abs.).
t_1 t_2 = boiling points of pure components (°C. abs. at 760 mm.).
A B = constants in the vapour pressure equation.
n = number of theoretical bubble-plates.
R = reflux ratio.
= mols. overflow from plate to plate, in the rectifying section of the column, per unit mol. product.
P = vapour pressure, mms. Hg. at temperature T.
θ = difference between the boiling point of an individual component, and the cut-point temperature.
$= \frac{1}{2}(t_2 - t_1)$
a = empirical constant.
Cut point = average boiling point of underlap-overlap.
= temperature at which the same percentage overhead is obtainable by standard column distillation.
$= \frac{1}{2}(t_2 + t_1)$.

COMPARISON OF VARIOUS FRACTIONATION CONDITIONS.

A variety of apparatus, both on the large scale and in the laboratory, is used for the distillation of petroleum. One unit may employ a large number of bubble-plates at a low reflux ratio; another may have a smaller number of plates at a higher reflux ratio; and the products from both may be equally well fractionated. Such units may be operated continuously on the flash vaporisation system; but it is possible to duplicate the results more or less closely in the laboratory using batch distillation.

It is evident that a correlative index, or coefficient, embodying the main variables of number of plates, reflux ratio, and system of distillation (whether batch, or continuous) would greatly facilitate the comparison of fractionating conditions; and would characterise

* Paper received March 28, 1933.

the degree of separation attainable in a given apparatus operated in a given manner.

Criteria of Degree of Separation Effected.

Frequently the gapping between the A.S.T.M. final boiling point, and the A.S.T.M. initial boiling point, of consecutive fractions is quoted. If, however, the I.B.P. is determined by means of a standard column distillation,[1] a much lower I.B.P. is found. Similarly the F.B.P. is dependent upon the amount of material tested and the manner of test.

Another method of expressing the degree of separation obtainable, is by reference to the difference between the A.S.T.M. end-point, and the cut temperature by standard column distillation of the same fraction.

In the case of equilibrium flash vaporisation,[2] the percentage of material in the distillate which boils below the flash vaporisation temperature, may be quoted.

It will be apparent that the above-mentioned criteria are dependent not only on the distillation system used, but also on the method of testing the products, the boiling range of the oils, the shape of the distillation curve of the material being distilled, the temperature of distillation, and other factors.

The criterion sought is in the nature of an apparatus constant, reflecting the effect of number of plates, reflux ratio, and system of distillation. It is deduced in this article, by a consideration of overlap and underlap volumes, that such a coefficient is experimentally observable and has physical significance.

Basis of Calculation.

The factors which control the degree of separation obtainable are chiefly :—

(1) Type of distillation apparatus.

(2) Number of bubble-plates.

(3) Reflux ratio.

(4) Boiling range, and shape of distillation curve, of material being distilled.

(5) Nature of oil being distilled.

(6) Temperature of cut-point (*i.e.*, average boiling point of overlap-underlap).

(7) Distillation temperatures obtaining in the system used.

[1] Peters, *Ind. Eng. Chem.*, 1926, **18**, 69.
[2] Leslie and Good, *Ind. Eng. Chem.*, 1927, **19**, 453.

In order to eliminate the variables 4, 5 and 6, it is proposed to calculate for the following hypothetical mixture :—

One ml. of each of 400 components, boiling at 1° C. intervals between 0° C. and 400° C., all obeying Raoult's Law.

Mol per cent. the same as volume per cent.

Distilled in all cases to 50 per cent. overhead and 50 per cent. residue.

By this means the effect of variable 7 also is largely but not completely standardised. The effect of column hold-up is assumed to be of negligible proportions.

The distillation systems envisaged are :—

(*a*) Flash vaporisation.

(*b*) Continuous column distillation.

(*c*) Batch distillation.

By the term " overlap " is meant the volume in ml. of material in 200 ml. distillate boiling above 200° C. (the cut-point temperature), and by " underlap " the volume in 200 ml. residue boiling below this temperature. It will be evident that the two volumes will be equal. For the purposes of this theoretical comparison the volume is called the " overlap coefficient."

Equilibrium Flash Vapourisation.

For a two-component system, the relation between the mol fraction lighter in the vapour, and that in the liquid, is given by the equation

$$y = \frac{Kx}{1+x\,(K-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

If 0·5 mol fraction is vapourised from an equimolecular feed mixture, equation 1 is simultaneous with the equation

$$x+y = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Hence

$$x = \frac{1}{1+K} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The term K may, however, be expressed as a temperature. The vapour pressure curves of hydrocarbons are of the type[3]

$$\log_{10} P = A - B\,\frac{t}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where A and B are constant for a group of hydrocarbons over a restricted temperature range.

[3] Meyer, *J. Inst. Petr. Techn.*, 1931, 17, 42.

Hence

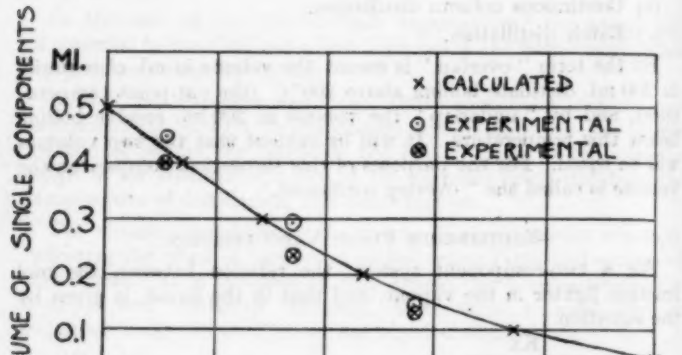
$$\log_{10} K = B\frac{(t_2-t_1)}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Now $t_2-t_1=2\theta$ ..... (6)

Hence combining equations 3, 5, and 6,

$$\theta = \frac{T}{B}\log_{10}\frac{1-x}{x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Equation 7 gives the mol fraction lighter component in the residue, when an equimolal mixture of two components boiling at $\theta°$ C. above and below the cut point (200° C. for the hypothetical mixture assumed) is flash vapourised into equal amounts of overhead and residue.



GRAPH 1.

COMPOSITION OF UNDERLAP AND OVERLAP IN PRODUCTS FROM EQUILIBRIUM FLASH VAPORISATION.

A curve of equation 7 is shown in graph 1. Now assuming Raoult's Law each pair of twin components boiling at $200\pm\theta°$ C. will be distributed according to graph 1; and the total volume of underlap per 200 ml. residue from the hypothetical mixture, will be given by the area under the curve.

Equation 7 integrated in the ordinary way gives the area as

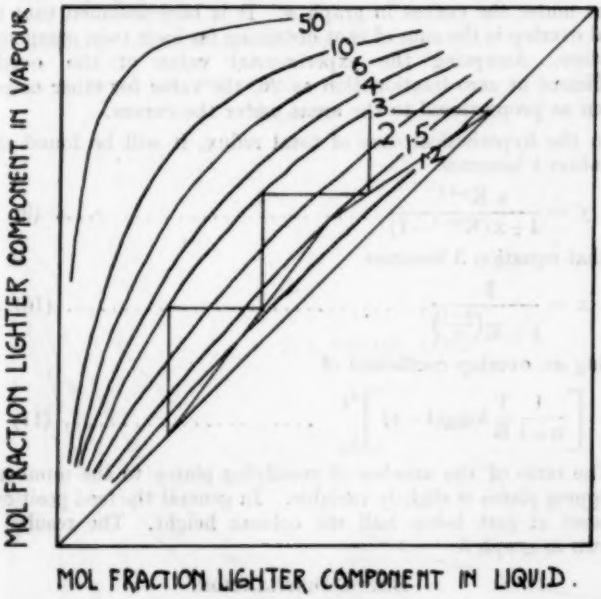
$$\left[\frac{T}{B}\log_{10}(1-x)\right]_{x_1}^{x_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

When $\theta=200°$ C., $x_2=0{\cdot}013$; so that evaluating between the limits $x_1=0{\cdot}5$ and $x_2=0{\cdot}013$, and taking T as 200° C. or 473° abs. and B as 4·9, the volume of overlap or underlap per 200 ml. distillate (*i.e.*, the overlap coefficient) works out at 28·5.

It is shown later that experimental results show a value of 26 for a number of crude oils of wide boiling range flash vapourised at temperatures between 300° F. and 500° F.

Continuous Fractional Distillation.

In this system the feed is introduced into the column at a suitable height; the bubble plates above serve to fractionate the



Graph 2.

McCabe and Thiele's method.

overhead, while the lower plates serve for residue stripping. The reboiler at the column base supplies vapour for product and reflux.

For two-component systems the graphical method of McCabe and Thiele[4] accurately represents the conditions. The overlap

[4] McCabe and Thiele, *Ind. Eng. Chem.*, 1925, 17, 605.

coefficient for the hypothetical mixture under consideration may be calculated in the following stages.

A series of curves representing equation 1 is prepared, as in graph 2. This is explored by the McCabe and Thiele method, assuming an equimolecular feed mixture separated into equal amounts of overhead and residue. The number of plates is noted, and the data plots as in graph 3. This graph is re-drawn to give graph 4, which is of the same type as graph 1. No advantage is here gained by the substitution of K by θ as in equation 7; the curves are readily plotted against log K, which is in linear relationship with θ.

The overlap coefficient is found by evaluating graphically the areas under the curves in graph 4. It is here assumed that the total overlap is the sum of that obtaining for each twin-component mixture. Accepting the experimental value of the overlap coefficient at zero fractionation as 26, the value for other cases is taken as proportional to the areas under the curves.

In the hypothetical case of total reflux, it will be found that equation 1 becomes

$$y = \frac{x\,K^{n+1}}{1+x\,(K^{n+1}-1)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

so that equation 3 becomes

$$x = \frac{1}{1+K^{\left(\frac{n+1}{2}\right)}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

giving an overlap coefficient of

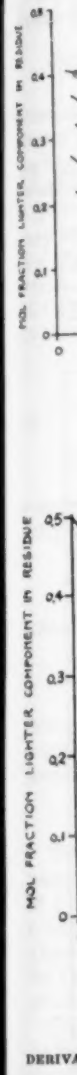
$$\left[\frac{1}{n+1}\,\frac{T}{B}\log_{10}(1-x)\right]_{x_1}^{x_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

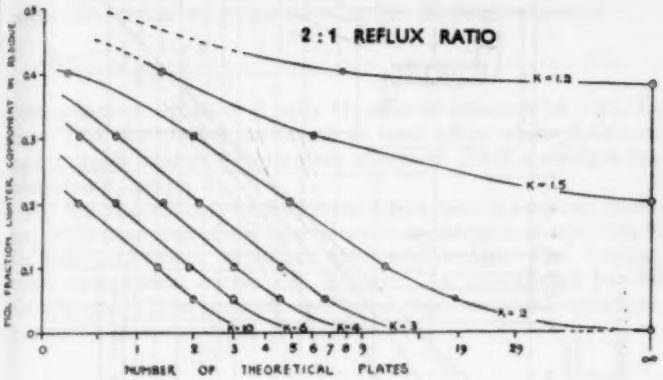
The ratio of the number of rectifying plates to the number of stripping plates is slightly variable. In general the feed position is located at just below half the column height. The results are shown in graph 5.

Batch Distillation.

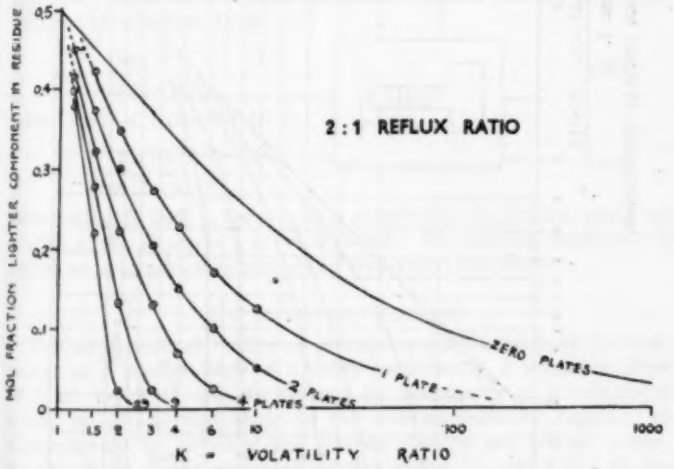
For a two-component system the result of batch distillation is given by the Rayleigh equation. Using equation 1 to correlate the vapour-liquid equilibrium, and applying to an equimolal mixture which is distilled without fractionation into equal amounts of overhead and residue, the Rayleigh integral is

$$K = \frac{\log x}{\log\,(1-x)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$





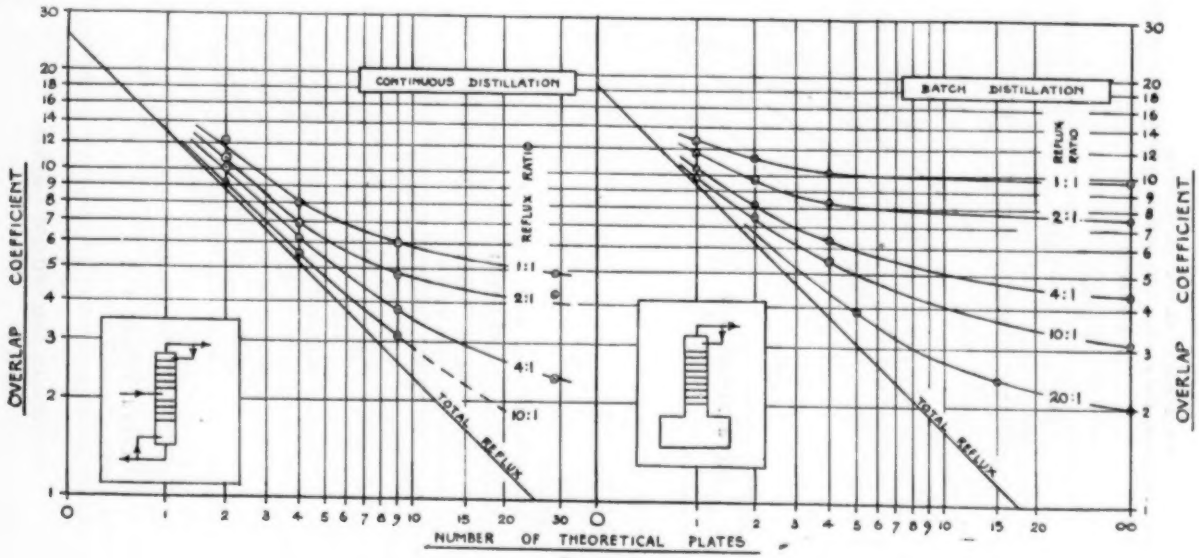
GRAPH 3.



GRAPH 4.

GRAPHS 3, 4.

DERIVATION OF OVERLAP COMPOSITION CURVES FOR SPECIFIED CONDITIONS OF CONTINUOUS COLUMN DISTILLATION.



GRAPH 5.

CALCULATED VALUES OF THE OVERLAP COEFFICIENT.

Where operating with n plates at total reflux, equation 9 is applicable, giving on integration in the Rayleigh equation

$$K^{n+1} = \frac{\log x}{\log (1-x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

Comparison of equation 8 with 11, also of equation 12 with 13, shows that the overlap coefficient at total reflux when plotted on log-log paper against the number of plates, gives a straight-line relationship (graph 5).

For the intermediate case of finite reflux ratio it becomes necessary to find an expression equivalent to equation 1 or equation 9. No simple formula expresses this relationship. The vapour-liquid composition curves can, however, be constructed by the McCabe and Thiele method, and fitted with empirical equations. It is found that equations of the type

$$y = \frac{ax}{1+x\,(a-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

or

$$y = \frac{x-x^2+ax}{1+x\,(a-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

represent most cases with sufficient accuracy. The Rayleigh integral of equation 14 is

$$a = \frac{\log x}{\log (1-x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

while that of equation 15 is

$$a = \frac{\log 2x}{\log (1-x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

Correlating K with a for specified distillation conditions, and then a with x, the K *versus* x curve is found. The overlap coefficient is found as before by estimating the area under the curve.

Experimental Results.

The experimental results of petroleum distillation may be compared on a similar basis of overlap coefficient. A reference slope of 1 ml. per 1° C. may be realised by calculating on a volume of crude oil giving this slope in the overlap-underlap region; or alternatively by dividing the overlap volume per 100 ml. crude, by the slope of the standard column curve (% per 1° C.) of the crude oil in the cut-point region.

The amount and boiling range of the overlap and underlap may be found with fair precision by standard column distillations of the distillate and residue respectively.

The extent to which the volume and boiling range of the overlap is affected by the amount vapourised from the crude will be evident from the experimental results. It might be anticipated that the amount of material in a crude oil which boils outside the observable boiling range of underlap or overlap, will affect neither the volume nor the boiling range of the overlap ; in which case the separation into overlap and underlap is similar to the twin-component system theoretically considered, provided that the oil has an approximately straight line distillation curve in the cut-point region.

No systematic figures for the fractionation of petroleum appear to be available in the literature. Extensive data on equilibrium flash vapourisation has, however, been recorded by Leslie and Good[2] and by Fancher[5].

The following results were found by Fancher, for Mid-Continent crude :—

Flash vap. temp. ° F.	Per cent. distillate.
300	15·0
400	37·5
500	53·0

From the graphs published the following data is read :—

Flash vap. temp. ° F.	Cut point. ° F.	Per cent. overlap in distillate.	Per cent. underlap in residue.
300	263	33·0	6·0
400	422	15·5	10·0
500	525	15·0	12·5

Hence the volumes of overlap and underlap, per 100 ml. crude, calculate as follows :—

Flash vap. temp. ° F.	Ml. overlap.	Ml. underlap.
300	15·0% × 33·0% = 5·0	85·0% × 6·0% = 5·1
400	37·5% × 15·5% = 5·8	62·5% × 10·0% = 6·3
500	53·0% × 15·0% = 7·9	47·0% × 12·5% = 5·9

Allowing for the experimental error of the standard column curves, it is seen that the overlap-underlap volumes are reasonably equal. The value of the overlap coefficient calculates as follows :—

Flash vap. temp. ° F.	Slope of standard column curve of crude oil in cut point region. Per cent. per 1°C.	Average of overlap-underlap volumes.	Overlap coefficient.
300	0·22	5·05	23·0
400	0·26	6·05	23·3
500	0·28	6·9	24·6

[5] Fancher, *Petr. Eng.*, 1931, **2** (6), 176.

TABLE I.

	Flash vap. temp. °F.	Per cent. distillate by flash vap.	Cut-point temp. °F.	Per cent. in distillate boiling above cut-point.	Per cent. in residue boiling below cut-point.	Ml. overlap per 100 ml. crude.	Ml. underlap per 100 ml. crude.	Average volume of overlap and underlap. Ml.	Slope of standard column curve of feed at cut-point. Ml. per 1° C.	Overlap coefficient.
Leslie and Good—Cabin Creek crude	250	8·5	175	48	3·5	4·1	3·2	3·7	—	13·7
	300	19·05	250	35	7·5	7·0	6·0	6·5	—	24·0
	350	32·80	333	22	10·5	7·2	7·0	7·1	Average	29·3
	400	44·22	410	16	11·5	7·1	6·4	6·8	0·27	25·1
	450	54·06	(485)	14	(14·5)	7·6	6·7	7·2	—	29·6
	500	64·07	(550)	11	(16)	7·0	5·8	6·4	—	23·7
Fancher—Inglewood crude	400	7·5	300	46	3	3·45	2·8	3·1	0·12	25·8
	450	13·0	390	32	4·5	4·15	3·9	4·0	0·15	26·7
	500	20·0	465	27	8	5·4	6·4	5·9	0·22	26·8
Fancher—Mid-Continent crude	300	15·0	263	33	6	5·0	5·1	5·05	0·22	23·0
	350	25·0	335	26	8·5	6·5	6·4	6·5	0·24	27·1
	400	37·5	422	15·5	10	5·8	6·3	6·06	0·26	23·3
	450	46·0	477	14·5	12	6·7	6·5	6·6	0·27	24·5
	500	53·0	(525)	(15)	(12·5)	7·9	5·9	6·9	0·28	24·6
Fancher—Shell-still P.D.	350	26·0	340	34	13	8·8	9·6	9·2	0·36	25·6
	400	50·0	430	29	25	14·5	12·5	13·5	0·62	21·7
Fancher—Pipe-still P.D.	250	22·0	220	35	7·5	7	5·8	6·4	0·29	22·1
	300	38·0	310	25	15	9·5	9·3	9·4	0·38	24·8
	350	58·0	390	22	23	12·7	9·7	11·2	0·47	23·8
	400	86·0	493	12	47	10·3	6·6	8·5	0·43	19·8

( ) Denotes extrapolated figures.

These results, together with others by the same investigator, and those of Leslie and Good, are detailed in Table I.

Reviewing these results, it will be seen that the overlap-underlap volumes tally fairly well; the figures for the former totalling 147·7 ml., while those for the latter total 131·9 ml. Allowing for experimental error, etc., the assumption in regard to the accuracy of the standard column distillation method would appear correct.

Regarding the overlap coefficient, the following observations may be made :—

(*a*) From the method of determination, its value will be zero at 0 per cent. and 100 per cent. vapourisation. This contributes to the low values recorded at the beginning of the crude oil series, and at the end of the pressure distillate series. The boiling range of the overlap is here limited by that of the feed stock.

(*b*) The tendency towards slightly lower values for the pressure distillates may be similarly explained.

(*c*) For a wide boiling range stock, the coefficient is not appreciably affected either by percentage vapourised, or by cut-point temperature, or by distillation temperature, and is sensibly constant at an average value of 26.

The experimental findings in paragraph (*c*) suggest that the volume and boiling range of the overlap are not affected by material boiling outside the boiling range of the overlap-underlap. Further evidence supporting this view is shown in graph 6. Here the "heads" of the residues and the "tails" of the distillates, for Leslie and Good's Cabin Creek Crude Oil results are plotted. The crude had almost a straight-line distillation curve of slope 0·27 ml. per 1° C., so that by considering 370 ml. crude, the reference slope of 1 ml. per 1° C. at cut-point is realised. The temperature scale is the difference between the boiling point of the underlap, or overlap, and the cut-point temperature. It will be seen that the curves for 350°, 400°, 450° and 500° F. vapourisation are nearly coincident. Moreover, the two curves are approximately symmetrical.

Composition of Overlap.

Assuming that the oil consisted of individual components boiling 1° C. apart, the composition of the overlap and underlap can be calculated from the data in graph 6.

Between 0°–50° F. divergence from cut-point, there are 26·5–14·0=12·5 ml. distilling in the distillate overlap. The mean

boiling point† of this group of components is 25° F.=14° C., and the average amount per 1° C. is 12·5 × 1·8/50=0·45 ml. of component. Graph 6 analysed in this manner gives the following results :—

Group	0–50° F.	50–100° F.	100–150° F.
	ml.	ml.	ml.
Overlap vol.	12·5	8·0	4·0
Ml. per 1° C.	0·45	0·29	0·14
Mean Boiling Point† ..	14° C.	42° C.	70° C.
	ml.	ml.	ml.
Underlap vol.	11·0	6·5	3·5
Ml. per 1° C.	0·40	0·23	0·13
Mean Boiling Point† ..	14° C.	42° C.	70° C.

These results are plotted on graph 1. This graph is the differential of graph 6, the overlap coefficient being found by evaluating the area under the curve. The calculated curve in graph 6 assumes the constants T, B, in equation 7 to have the values of 400° F. (477° C. abs.) and 4·9 respectively. Bearing in mind that the calculated results are for molecular fraction, and that the vapour pressure equation 4 is an approximation, the agreement is good. The experimental results indicate that the volume of overlap boiling 200° F. or more away from the cut point, is negligibly small. At this degree of divergence from the cut-point the experimental results tend to tail off more rapidly than corresponds with equation 7.

At 200° F. divergence x in equation 7 has a value of approximately 0·07. Taking representative temperatures from Table I., and evaluating equation 8 between the limits x=0·5 and x=0·07, the calculated value of the overlap coefficient for equilibrium flash vapourisation is given in Table II. :—

TABLE II.

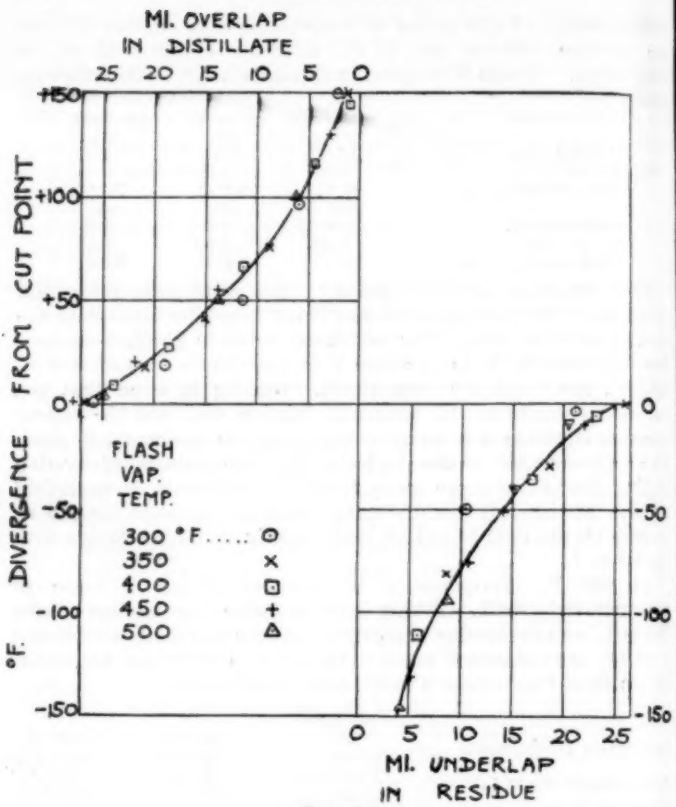
Distillation Temperature ..	300° F. (149° C.)	400° F. (204° C.)	500° F. (260° C.)
Approximate Cut Point ..	250° F. (121° C.)	420° F. (216 °C.)	550° F. (288° C.)
Value of B for hydrocarbons boiling at cut point temperature	4·8	4·9	5·4
Overlap Coefficient	23·8	26·3	26·7

It is apparent that the overlap coefficient is no simple function of T or B alone, and that the relative constancy is to some extent fortuitous. The values tally satisfactorily with the observed values in Table I., including the slightly lower value at 300° F.

REVIEW.

The theoretical investigations dealt with a straight-line boiling mixture distilled into 50 per cent. overhead and 50 per cent. residue.

† *i.e.*, divergence in b. pt. of component from the mid-point of overlap—underlap.



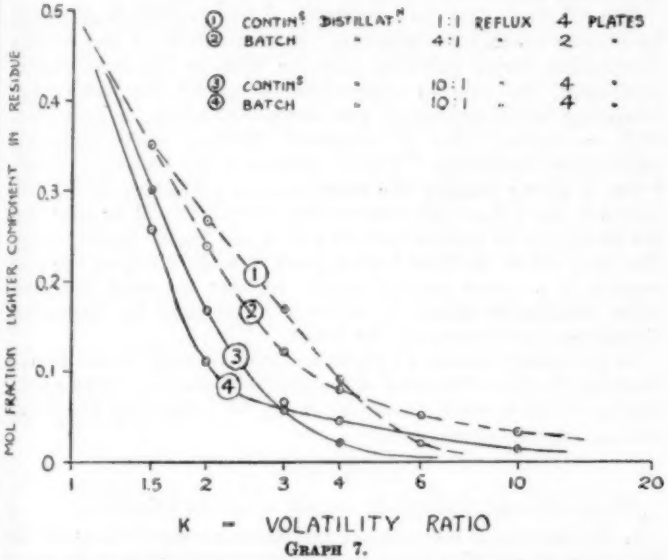
GRAPH 6.

STANDARD COLUMN DISTILLATION CURVES, LIGHT ENDS IN RESIDUE AND HEAVY ENDS IN DISTILLATE FROM EQUILIBRIUM FLASH VAPORISATION. PER 370 ML. CRUDE OIL.

The experimental results indicate, however, that material boiling outside the observable boiling range of overlap-underlap does not affect the volume or boiling range of the overlap-underlap. It follows, therefore, that any separation by distillation, whether into 10 per cent. or into 90 per cent. overhead, may be regarded as a twin-component system in the cut-point region vapourised to 50 per cent. overhead, provided that the boiling range of the overlap is not limited by that of the feed-stock, and that the feed-stock shows an approximately straight-line distillation curve in the cut-

point region. The concept of overlap coefficient should therefore be of general applicability.

The case of continuous distillation considered is, of course, the simple ideal case. In practice a plant layout may not be so simple, but the foregoing line of approach may be found applicable. The effect of fractionation being to narrow down the volume and boiling range of overlap, the concept of an overlap coefficient



GRAPH 7.

COMPARISON OF OVERLAP COMPOSITION CURVES BY BATCH AND CONTINUOUS DISTILLATION.

may be as applicable to a well fractionated narrow cut as to an unfractionated one; provided that the observable boiling range of the overlap is not limited by that of the feed material, and that the cutting is not so sharp as to isolate pure components.

It has been assumed that the mixture undergoing distillation possesses a straight-line distillation curve over the cut-point region. Actually a number of the oils quoted in Table I. showed an appreciable curvature in the cut-point region, but gave representative results for the co-efficient. It appears, therefore, that the average slope in the cut-point region is sufficiently informative.

The range of petroleum oils for which experimental results are shown in Table I. does not preclude the existence of mixtures

which deviate from Raoult's Law and which give abnormal values of the coefficient. It is possible, however, that the deviation is expressible as a percentage correction to the coefficient.

Except as above noted, the coefficient in the case of a commercial unit should be determinable by standard column assays of the products. In comparing results with the theoretical figures, allowance should, of course, be made for the fact that a plate is in practice less efficient than a theoretical plate.

Graph 5 shows that the same degree of fractionation is attainable by diverse operating conditions. A comparison of the overlap composition curves indicates, however, that for the same overlap co-efficient, the overlap composition is nearly the same when comparing batch distillation with batch distillation, or continuous with continuous; but is somewhat different when comparing batch with continuous. This is illustrated by graph 7; curves 1 and 2 giving roughly the same overlap coefficient of 8, while curves 3 and 4 have the same value of 5·6. It will be seen that the batch curves have a heavier tail in the higher boiling range. This may affect the final boiling point of a distillate, or the gum content of a re-run cracked spirit. Strictly speaking, therefore, batch distillation cannot be accurately simulated by continuous distillation, nor continuous by batch.

As previously stated, no published experimental results appear available for closer checking of the results in graph 5. The results relative to each other should, however, be correct for the hypothetical mixture considered.

Conclusions.

The conclusions tentatively arrived at are as follows:—

1. The amount of material in a petroleum mixture boiling outside the observable boiling range of overlap-underlap, does not affect the volume of the overlap or underlap, and does not affect the degree of separation obtainable by distillation.

2. A numerical expression of the degree of fractionation is possible.

3. Selection of the economic compromise between the reflux ratio and number of plates is facilitated.

4. The more plates a column has, the higher is the reflux ratio necessary to make full use of the plates.

5. At high reflux ratio, for the same number of plates batch distillation gives sharper cutting than does continuous. At commercially practicable reflux ratios, however, continuous distillation shows a marked advantage.

6. Continuous distillation cannot be accurately simulated by batch distillation.

Ozone, Knock-Inducer Extraordinary.*

By Donald B. Brooks.

The Observed Effect.

In connection with a research on engine exhaust products, a Cottrell precipitation apparatus was designed and constructed for attachment to the exhaust line. That contrariness so deeply ingrained in human nature suggested attaching it to the intake instead. This was done, using the detonation test engine recently developed by the Co-operative Fuel Research and adopted by the A.S.T.M. as standard for knock tests. With the precipitator attached, but not operative, the engine was adjusted to give average intensity of detonation (knockmeter reading of 45). When the current was turned on, the detonation became severe, and the knockmeter went off scale. The experiment was repeated, using a lighter initial knock, with the same result. Finally, with the least initial knock which would register on the meter, it was found possible to get a measurement of the detonation with the precipitator in action.

The question at once arose, is this something new, or is it some new phase of a well-known phenomenon? If new, to which of a half-dozen possible causes is it to be ascribed? Conceivably it might be caused by ionization, by the production of nitrogen oxides or ozone, by removal of dust particles, by heating, or by some secondary effect.

Qualitative Determination of the Cause.

The precipitator used for most of the tests is sketched in Fig. 1. It was in the form of a T, the run being of 2½ in. pipe and the branch of 1½ in. pipe, the latter ending in an enlargement suitable for coupling to the CFR carburettor. A tightly stretched copper wire was supported by insulators so as to pass centrally through the 2½ in. pipe.

A potential of up to 20,000 volts was applied between the wire and the 2½ in. pipe. This potential was obtained from an X-ray apparatus. Normally the wire was the positive side; if it were made negative, the effect was only a fraction as large. Use of an alternating current appeared to give nearly as large an effect on fuels as did direct current when the wire was positive.

That the effects observed were not caused by ionization was suggested by the fact that the size of the precipitator, or the length of tubing between it and the carburettor, did not materially affect the results. Also, the introduction of fine mesh copper

* Paper received August 15th, 1933. Publication approved by the Director of the Bureau of Standards of the U.S. Department of Commerce.

screening between the precipitator and the carburettor did not alter the effect on knock. To verify this further, a tube containing 15 millicuries of radon was placed in the air horn. The effect on detonation was not perceptible by ear. A statistical analysis of the knockmeter readings indicated a difference such as would occur about once in ten times by chance. It was concluded that the ionization produced in this manner affected the detonation to an extent equivalent to only a fraction of an octane unit, if at all.

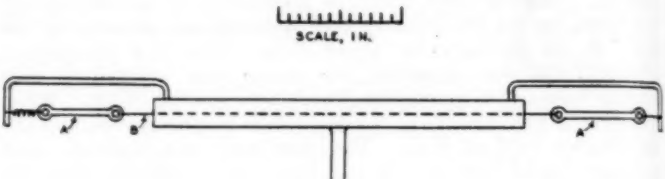


FIG. 1.

The possibility that the effects observed were caused by nitrogen oxides, heat generated, or removal of dust particles was next eliminated by using a small water-cooled precipitator, through which a stream of oxygen flowed, instead of the precipitator shown in Fig. 1. The product was caused to flow into the induction system at a slow, constant rate.

This additional oxygen, of course, materially increased the detonation; this effect was compensated by allowing the oxygen to continue flowing but with the precipitator inoperative, during a comparison test. The differential effect on detonation was of the same order of magnitude as when the brush discharge tube was employed.

The process of elimination thus pointing strongly to ozone as the cause of the phenomenon, it remained merely to demonstrate that ozone produced chemically had a like effect. For this purpose the reaction between nitric acid, HNO_3, and ammonium persulfate, $(NH_4)_2\ S_2O_8$, was chosen. The action of 15 grams of nitric acid on 20 grams of ammonium persulfate at 65 to 75° C. in an atmosphere of carbon dioxide produces oxygen and ozone. While the carbon dioxide normally is absorbed in alkali, in this instance it was used to convey the relatively small amount of oxygen plus ozone to the engine.

To isolate the effect of the ozone, it was necessary to run a "blank" test, using heat to decompose the ozone formed. When the ozone was so decomposed, the increase in detonation during the period of reaction (effect of oxygen alone) was equivalent to 5 octane units; when the ozone was not decomposed, the increase of detonation was equivalent to 8 octane units.

Quantitative Determination of the Effect of Ozone on the Detonation of Fuels.

Before passing to a discussion of the experiments, a brief description of apparatus and technique may be in order. All detonation tests were made on CFR engines coupled to synchronous motors; except as noted, these were operating under "Research Method" conditions. Chief among these conditions are: speed, 600 revolutions per minute; jacket temperature, 212° F.; throttle, fully opened; and intake temperature, that of the ambient air. For each fuel and change of conditions, the carburettor was carefully adjusted to give the maximum intensity of detonation. The compression ratio was, of course, varied to give an intensity of detonation suitable for knockmeter instrumentation.

In determining the effect of ozone on the detonation of a given fuel, the latter was caused to match various blends of the primary or secondary standards, or stable fuels of known octane number, by varying the potential applied to the precipitator. As this potential could be applied only by steps, the point of exact match could not be found directly. When a single reference fuel of known rating was used, the point of exact matching was estimated by interpolating between successive potential steps. When either primary or secondary standards were employed, the interpolation was made between different blends of the standards. The data appeared to justify linear interpolation in either case.

One of the first fuels studied was the secondary standard reference fuel C–6. This very stable fuel has a rating of 76·6 octane number by the Research Method, 76·1 by the Motor (now A.S.T.M.) Method. The data showing the effect of ozone on the detonation of this fuel are presented in Table I. and plotted in Fig. 2. It is apparent from either the table or the figure that the decrease of nearly 40 octane units in the knock-rating of C–6 is essentially linear.

Table II. illustrates the effect of ozone on a number of fuels. Although the determinations as made were in terms of potential applied to the precipitator (Fig. 1), the values have been expressed in terms of ozone concentration in per cent. by volume in the intake air. For reasons of economy the actual concentration of ozone was not determined for each test; instead a series of ozone

determinations was made at different applied potentials. From the calibration so obtained, ozone concentrations have been estimated for each test.

TABLE I.

Effect of Ozone on Fuel C-6.

Ozone in intake air. Thousandths of a per cent. by volume.	Octane number of fuel C-6.	Decrease. Octane units.	Decrease. Octane units per 0·001% ozone.
0·0	76·6	—	—
4·5	62·4	14·2	3·2
5·2	58·6	18·0	3·5
5·4	58·2	18·4	3·4
6·3	55·5	21·1	3·4
7·2	51·7	24·9	3·5
8·0	48·5	28·1	3·5
9·0	45·9	30·7	3·4
10·7	39·0	37·6	3·5

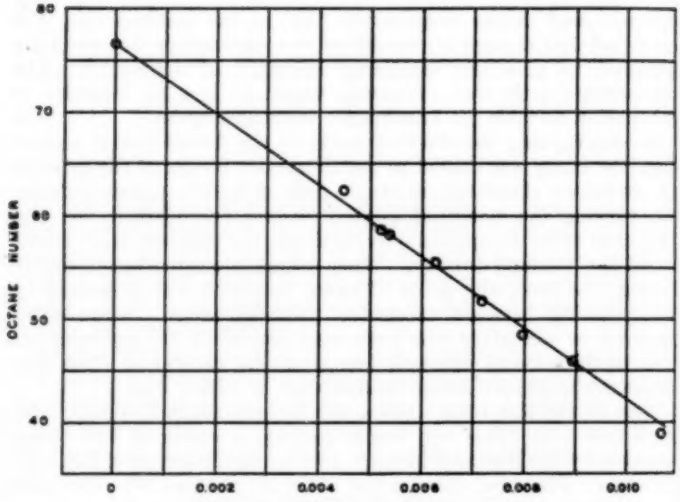


FIG. 2.

The values so obtained are believed to be reasonably accurate except in the case of Fuel A–2, Table II. The runs on this fuel were made nearly two months after the other runs had been completed, and atmospheric conditions, steady throughout the main period of tests, had altered very materially. That this change affected the concentration of ozone produced at a given potential was evidenced by the fact that at the time Fuel A–2 was

rated, a given potential applied to the precipitator caused only 0·4 the drop in rating of Fuel C–6 that had been found earlier. The ozone concentration given for Fuel A–2 was taken from the earlier calibration ; if the behaviour of Fuel C–6 be taken as a criterion, presumably the concentration of ozone in the test of Fuel A–2 was about 0·003 per cent., and its rate of decrease, 8 octane units per 0·001 per cent. ozone, rather than the figures given in Table II.

TABLE II.

Effect of Ozone on Various Fuels.

Fuel.	Octane number of fuel.	Ozone used. Thousandths of a per cent. by volume in intake air.	Octane number with ozone.	Decrease. Octane units per 0·001% ozone.
*A-2	48·5	7·07†	25·4	3·3†
*B-2	67·9	6·18	48·5	3·1
*C-6	76·6	See Table I.		(Av.) 3·46
60% C-6, 40% benzene	86·9	10·7	61·8	2·3
Cracked fuel RT-11	68·0	10·5	48·5	1·9
Cracked fuel RT-12	66·5	11·6	48·5	1·6
Commercial fuel A	66·1	9·5	48·5	1·8
Commercial fuel B	66·0	8·4	48·5	2·1
Commercial fuel C	63·5	6·3	48·5	2·4
Commercial fuel D	70·7	12·9	48·5	1·7
Cabin Creek gasoline	39·0	1·8	25·4	7·6
Cabin Creek gasoline	39·0	6·4	0·0	6·1
Texas spirits	25·4	5·5	0·0	4·6
C-6 plus 2 ml. $PbEt_4$ per gallon ..	90·2	7·7	76·6	1·8
C-6 plus 2 ml. $PbEt_4$ per gallon ..	90·2	11·1	67·9	2·0

*Secondary standard reference fuels. † See text.

The data of Table II. were analysed to determine the degree of connection between the decrease in octane rating per 0·001 per cent. ozone, and both (*a*) the normal octane rating of the fuel and (*b*) the response of the rating to change in severity of knock test conditions. The latter quantity, colloquially known as "depreciation," was measured by the difference of octane rating by the Research and Motor Methods.

The analysis for (*b*) showed a correlation coefficient of $-0{\cdot}29 \pm 0{\cdot}32$, which is too low a coefficient to be of any significance, as the probability of obtaining a coefficient equally large from random numbers is nearly one-half. That the less stable of the fuels tested were less affected by ozone is indicated, but no general relation of this sort is affirmed. The fuels tested, however, are not ideal for establishing such a relation. The fact that the two fuels composed in part of cracked gasoline gave very low rates of decrease of octane rating with ozone is at least noteworthy.

The analysis for (*a*) showed a correlation coefficient of $-0{\cdot}70 \pm 0{\cdot}25$, which has a random probability of less than one-fiftieth. This correlation is high enough to be of real significance, and indicates

an increasing effect, *in terms of octane units*, on fuels of lower octane number. This may also be interpreted as another indication that the "size" of an octane unit varies over the scale. A partial correlation was made for (*b*), thus eliminating the effect of the influence of octane rating on ozone response. This gave a coefficient even lower than was found in the total correlation for (*b*) above. Hence these data do not indicate any connection between ozone response and "depreciation."

A point of no especial importance except in so far as it illustrates the magnitude of the effect of ozone on detonation is that the rating of the Cabin Creek gasoline could have been reduced as much as 40 *octane units below heptane*, before reaching the limiting potential of the precipitator tube.

A study was also made to determine the "ozone equivalent" of the knock inhibitors, tetraethyl lead, benzene and absolute alcohol. To a quantity of Fuel A–2 was added 1 ml. of tetraethyl lead per gallon; other quantities were treated with sufficient benzene and sufficient alcohol to make blends equal in anti-knock value to the leaded sample. The octane number of the three fuels thus constituted was 59·6. The knock of each of these fuels was then caused to increase, by introduction of ozone in the intake air, until each successively matched each of four reference fuels, the first of which was untreated A–2. The values so obtained are listed in Table III. and plotted in Fig. 3. From these data it

TABLE III.

Effect of Ozone on Fuel A-2 *Doped to* 59·6 *Octane Number.*

Knock inhibitor.	Amount used.	Ozone. Thousandths of a per cent. by volume in intake air.	Octane number with ozone.	Decrease of rating octane units per 0·001% ozone.
$PbEt_4$	1 ml. per gal.	2·2	48·5	5·0
,,	,,	3·2	43·8	4·9
,,	,,	3·6	39·0	5·8
,,	,,	4·4	25·4	7·7
Benzene	19⅔%	3·0	48·5	3·8
,,	,,	4·3	43·8	3·7
,,	,,	4·4	39·0	4·7
,,	,,	5·4	25·4	6·4
Alcohol (Abs.)	9⅓%	3·6	48·5	3·1
,, (,,)	,,	4·5	43·8	3·5
,, (,,)	,,	5·5	39·0	3·8
,, (,,)	,,	6·4	25·4	5·3

can be seen that roughly 30 per cent. more ozone was required to annul the effect of the benzene than to annul that of the tetraethyl lead; 60 per cent. more ozone was required in the case of the alcohol blend than for the leaded fuel. Fig. 3 indicates that the effectiveness of ozone on each of these doped fuels increases with increasing proportion of ozone in the intake air.

As 0·00224 per cent. by volume of ozone in the intake air counteracted the effect of 1 ml. of tetraethyl lead per gallon in Fuel A–2, a simple computation shows that the ozone counteracted 1·4 times its weight of tetraethyl lead, in this case. It should be noted, however, that the specific effect of lead in increasing quantities decreases rapidly, whereas that of ozone, at least in the cases of these doped fuels, increases. The above ratio of 1·4 would therefore increase with higher concentrations of tetraethyl lead.

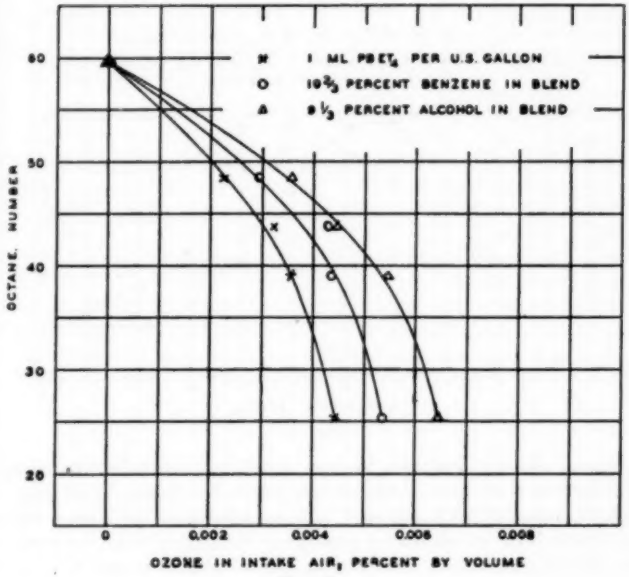


FIG. 3.

A phenomenon for which no satisfactory explanation has appeared is the richer air-fuel ratio required for maximum intensity of detonation when ozone is supplied. The curves of Fig. 4 illustrate this well. The detonation was measured using Fuel C–6, then for C–6 plus 1 ml. tetraethyl lead per gallon, lastly for the latter fuel with sufficient ozone to counteract the effect of the tetraethyl lead. These tests were all made under the same engine conditions ; however, the fuel flow for maximum detonation with C–6 plus lead was 17·9 ml. per minute, whereas when ozone was added the required flow was 21·3 ml. per minute.

Inasmuch as ozone is destroyed at elevated temperatures, and hence cannot, presumably, exert any effect after combustion has begun in the engine cylinder, it was thought that an effect analogous to that found in the experiments described above might be obtained by bubbling ozone through liquid fuel. Obviously the fuel used must be a pure compound, otherwise the effect sought would be complicated by volatilization of light ends during the bubbling

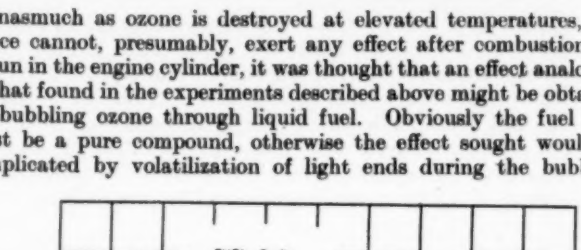


FIG. 4.

process. Merely because it was available, cyclohexane (hexamethylene) was used. Ozone prepared by brush discharge in oxygen was bubbled through the cyclohexane for about thirty minutes. This involved the passage of roughly 100 ml. 0_3 through the 500 ml. of liquid. On rating the resultant product, a value of 81·8 octane number was obtained, as compared with a simultaneous* value of 82·6 for untreated cyclohexane. The difference, although but little larger than the experimental error, appears from a statistical analysis of the knockmeter readings to have been real.

EFFECT OF OZONE ON POWER, EFFICIENCY AND SPARK ADVANCE.

On finding that a brush discharge in a Cottrell precipitator attached to the carburettor had a material effect on detonation,

* Obtained by use of the four-bowl C.F.R. carburettor. To rate two fuels simultaneously, they are placed in diagonally opposite bowls, with bracketing reference fuels in the remaining two bowls. Knockmeter readings are then taken on the fuels in rotation.

it was conjectured that some effect on power, economy or optimum spark advance might be detectable, using, of course, a fuel which did not detonate under the selected test conditions.

The first tests, made at a compression ratio of 4·0 on a CFR engine coupled to an electric dynamometer, appeared to confirm this idea. A loss of power of 2·5 per cent. was obtained, but with no loss of efficiency. No appreciable change in optimum spark advance was detected. Several interesting theories had to be discarded, however, when the power loss was later found to be caused solely by heating of the air in the brush discharge. Although the current in the discharge was less than 5 milliamperes, the maximum potential was of the order of 20 kilovolts ; the power was sufficient to raise the intake air temperature about 15° C.

A second series of tests was run later, during which the ozone was produced from oxygen, in a water-cooled brush discharge tube, and metered to the carburettor intake. With the brush discharge on, the maximum indicated horsepower was $3{\cdot}294 \pm 0{\cdot}003$; with brush discharge off, but with oxygen flowing at the same rate, the power was $3{\cdot}291 \pm 0{\cdot}002$. A series of tests to determine optimum spark advance gave the values 21·4 degrees with ozone, 21·9 degrees without. While probable errors were not computed for the latter, the difference is probably not significant. The ozone concentration used during this test series was 0·0045 per cent. by volume in the intake air. The additional oxygen supplied was 0·633 per cent. by volume in the intake air.

Conclusions.

Throughout the foregoing, the endeavour has been to present the facts and to avoid drawing conclusions. While quantitative data have been given in some cases, their exactness is not all that could be desired. The brush discharge method used in producing ozone, while simple and inexpensive, restricts the range to very small concentrations. However, it is believed that the following conclusions may be stated with assurance.

1. In ozone a new tool for the study of detonation and the testing of theories thereof has been discovered.

2. The effects of ozone and tetraethyl lead on fuels, while opposite, are of the same order of magnitude.

3. Different amounts of ozone are required to counteract an equal improvement in the anti-knock value of a fuel obtained by use of different knock inhibitors.

4. The detonation of different fuels is affected to a materially different degree by admixture of ozone in the intake air.

5. In the concentrations tried, ozone is without measurable effect on power, economy, or optimum spark advance.

It also appears that:—

1. The air-fuel ratio for maximum intensity of detonation may alter with admixture of ozone.

2. Treating liquid fuel with ozone causes its knock-rating to be decreased. The effect may be due only to dissolved ozone.

It is suggested that the following experiments might prove worth while:—

1. Treating liquid fuel with higher concentrations of ozone and for longer periods. If an effect much larger than that found herein is obtained, a chemical analysis should reveal the change causing the decreased octane-rating.

2. A study of the effect of ozone on Diesel engine performance.

A Contribution to the Study of Oil-Field Water Analysis.*

By Abol Hassan Khan Radjy, B.Sc. (Student Member), and Charles Edmund Wood, M.Sc., A.I.C. (Member).

Part III.† Estimation of Sodium by Dihydroxytartaric Acid.

In the analysis of oil-field waters it is customary to separate and weigh or estimate the alkali metals as chlorides or sulphates as a final stage in the quantitative estimation of the various radicles present, potassium being then estimated directly and sodium found by difference. Such a method leads to inaccuracy and cumulative error. The inaccuracies of the mixed chloride method for estimation of potassium and sodium are considered by Thresh and Beale.[1] Various methods for the direct estimation of sodium have been proposed which depend upon the sparingly soluble nature either of the sodium salt of a complex acid or of a co-ordination sodium compound. The more important methods include the use of dihydroxytartaric acid, zinc uranyl acetate, magnesium uranyl acetate, cobalt uranyl acetate, nickel uranyl acetate and of uranyl acetate itself.[2] The pyroantimonate method[3] has been critically studied by Balint,[4] and the butyl alcohol ethyl acetate process, in which mixture of organic reagents, sodium perchlorate is soluble was investigated by Smith and his collaborators,[5] and an account of the pyrosulphate method is given by Gooch.[6] Further, for qualitative detection of sodium the following are important, fluoboric and fluosilicic acids,[7] oxalic acid,[8] lithium ferro-cyanide[9] and potassium pyroantimonate.[10]

Dihydroxytartaric Acid, Its Salts and Their Estimation.

The acid which was first obtained by Gruber[11] was investigated by Kekule,[12] who assigned a diketonic structure to the dibasic

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* Paper received August 2nd, 1933.

† For Parts I. and II., see *J. Inst. Petr. Techn.*, 1932, **18**, 817.

[1] "The Examination of Waters and Water Supplies," 3rd edition, 1925 p. 341.

[2] *Cf.* "Organic Reagents for Metals," Hopkins and Williams, 1933.

[3] Leenwerr, *Chem. Weekblad.*, 1919, **16**, 1424; Tomula, *Zeit Anorg. Chem.*, 1921, **118**, 81.

[4] *Zeit. Biochem.*, 1924, **150**, 424.

[5] Willard and Smith, *J. Am. Chem. Soc.*, 1922, **44**, 2816; Smith, ibid., 1925, **47**, 762; Smith and Ross, ibid., 1925, **47**, 774, 1020.

[6] "Methods in Chemical Analysis," 1912, p. 79.

[7] Mathers, Stewart, Housemann and Lee, *J. Am. Chem. Soc.*, 1915, **37**, 1515.

[8] Winkler, *Pharm. Zeutralhalle*, 1925, **66**, 669.

[9] Faustino Diaz De Rada, *Anales Soc. Espan.*, 1926, **24**, 442.

[10] Treadwell, "Analytical Chemistry," Vol. I, p. 83.

[11] *Ber.*, 1879, **12**, 514.

[12] *Annalen*, 1883, **221**, 245.

acid. Eleven years later Fenton[13] prepared the acid, re-investigated its constitution, and by a series of refined and interesting experiments he concluded that the compound was an unstable tetrahydroxydicarboxylic acid ($COOH \cdot C(OH)_2 \cdot C(OH)_2 \cdot COOH$). Further investigation showed that the sodium salt was sparingly soluble, and that both the acid and sodium salt could be titrated quantitatively with potassium permanganate in accordance with the generalised equation $C_4H_6O_8+3O=4CO_2+3H_2O$.[14] This author titrates both the acid and its salts directly, but direct titration presents considerable difficulty, for the rate of reaction of potassium permanganate with dihydroxytartaric acid is slow and the pink colour of the permanganate is persistent, thus making the estimation very lengthy and liable to error. Fenton was able to precipitate sodium as the dihydroxytartrate and estimate it to about 1 per cent. negative error. The following data showing the order of accuracy are selected from his results :—

Sodium chloride taken.	Na found.	Na calculated.
0·2814 gram ..	0·0966 ..	0·975
0·200 ,, ..	0·0776 ..	0·0786

His method was to neutralise the acid with sodium-free potassium carbonate, and to this solution the sodium as chloride was added; after standing, the precipitate was filtered off under reduced pressure, dissolved in dilute sulphuric acid and titrated with potassium permanganate at room temperature. The reaction volume in which precipitation took place is not given. Fenton states that metals other than potassium and magnesium must be absent and that ammonium salts cause low results, thus dihydroxytartaric acid should be neutralised with potassium carbonate and not with ammonia for preparing the precipitating reagent. According to Fenton, magnesium has no effect on the estimation and full data for the influence of ammonium salts are not given. A point of interest about the present research is that both factors have been studied in detail.

Lachmann[15] has investigated further the properties of the acid and its sodium salt, and draws attention to the structural resemblance of this acid to benzil. He discussed and published data which developed the method originated by Fenton, and mentions that there are irregularities in the action of potassium

[13] *J.C.S.*, 1894, **65**, 901.

[14] Fenton, *J.C.S.*, 1898, **73**, 167; 1898, **74**, 71; Fenton and Ryffell, ibid., 1902, **81**, 426; Fenton, ibid., 1905, **87**, 813.

[15] *J. Am. Chem. Soc.*, 1921, **43**, 2091.

permanganate due to the formation of tartronic acid in accordance with the following equation :—

$$COOH \cdot C(OH)_2 \cdot C(OH)_2 \cdot COOH = COOH \cdot CH(OH) \cdot COOH + CO_2 + H_2O,$$

with simultaneous loss of carbon monoxide or formaldehyde. Lachmann found that dihydroxytartaric acid, freshly made and kept cool, used exactly six oxygen equivalents, but a similar solution after heating until all the dihydroxytartaric acid had been converted into tartronic acid required little more than four equivalents. This can only be accounted for by a profound change in which carbon monoxide or formaldehyde is removed from reaction ; these points explain Lachmann's conclusion.

Six equivalents of oxygen are necessary to oxidise dihydroxytartaric acid and six equivalents of oxygen are also necessary to oxidise tartronic acid to carbon dioxide and water. $COOH \cdot CH(OH) \cdot COOH + 3O = 3CO_2 + 2H_2O$. The present authors suggest the following mechanism for transformation of dihydroxytartaric acid to tartronic acid.

$$COOH \cdot C(OH)_2 \cdot C(OH)_2 \cdot COOH = [COOH - C(OH)_2 - C(OH)_2H] + CO_2$$
$$[COOH \cdot C(OH)_2 \cdot C(OH)_2H] = COOH \cdot CH(OH) \cdot COOH + H_2O.$$

The intermediate compound in these equations is potentially ketonic and aldehydic and undergoes auto-oxidation. The aldehydic group is capable of reducing the ketonic to a secondary alcoholic group and at the same time being oxidised to a carboxyl group, the result being the formation of tartronic acid.

Lachmann's method of estimation is to separate the insoluble sodium dihydroxytartrate and, owing to the irregularities of oxidation by potassium permanganate, mentioned previously, he uses in the first instance alkaline potassium permanganate. The reaction mixture is boiled for a few minutes, cooled slightly, then acidified with dilute sulphuric acid and the excess of permanganate titrated with oxalic acid. The solution was boiled during the titration until the precipitated manganese dioxide had gone into solution, on cooling, excess of oxalic acid was titrated with permanganate. There are many disturbing features regarding this mode of titration. One of the points of interest of Lachmann's work is that direct titration with potassium permanganate of sodium dihydroxytartrate after boiling with dilute sulphuric acid gave very low results.

Oktav[16] carried out a series of experiments on the solubility of sodium dihydroxytartrate and on the estimation of sodium. His

[16] *J. Rus. Chem. Phys. Soc.*, 1928, **60**, 661.

experiments on the latter were carried out on similar lines to those employed by Fenton. In general he found the method satisfactory.

Solubility of Salts.—The acid is eminently satisfactory for the determination of sodium owing to the very low solubility of its normal sodium salt. The solubility at different temperatures is given below :—

Temperature.		Parts of salt dissolved by 100 parts of water.
0° C.	..	0·039 (Fenton)
5° C.	..	0·042 (present authors)
10° C.	..	0·053 (Oktav)

Certain of its salts with metals other than sodium are also sparingly soluble,[17] and generally it is desirable that all metallic radicles except ammonium and magnesium should be removed before estimating sodium by this method. The solubility of certain salts of dihydroxytartaric acid has been investigated by Fenton,[18] and the following data are taken from his work. It is to be noted that the solubilities of the salts of the alkalies increases with increasing atomic weight, lithium the first member of the alkali series being exceptional :—

Metal.		Parts of salt soluble in 100 parts water at 0° C.
Cæsium	..	22·5
Rubidium	..	6·5
Ammonium	..	2·8
Potassium	..	2·7
Lithium	..	0·08

Acidic Radicles.—The acid radicles present should be either chlorides, sulphates or nitrates. The present research has been carried out in the presence of chloride, sulphate being present only in the case of the influence of magnesium on precipitation. If hydroxides or carbonates are present they may be neutralised with hydrochloric acid. Acetates and phosphates tend to give low values for sodium, and should be eliminated before precipitation with potassium dihydroxytartrate. Apparently borates give anomalous results.

Difficulties in Previous Methods.—(1) In direct titration of the sodium salt the permanganate colour is persistent especially towards the end point and takes several minutes to discharge after each addition. Further, decomposition of the unstable acid and salt may take place during the lengthy time of titration. (2) Using excess of permanganate which can be back titrated with oxalic acid requires heat which causes precipitation of hydrated manganese dioxide, so that a sharp and accurate end point cannot be obtained. (3) Initial alkaline oxidation and subsequent acid

[17] Cf. Fenton.
[18] *Loc. cit.*

oxidation and back titration is not a clean, straightforward method and leads to inherent errors. (4) Working details employed with respect to precipitation, filtration, working temperature, reaction volume, solubility of sodium salt, correlation of percentage error, exact influence of ammonium and magnesium salts and catalysts for promoting oxidation in the cold are frequently not properly described or even omitted, and in order to rectify these omittances the following work was undertaken.

Catalysts for Accelerating the Oxidation of Dihydroxytartaric Acid.

Manganese Sulphate.—The catalytic action of manganous sulphate on the rate of decomposition of dihydroxytartaric acid in the presence of an exact amount of potassium permanganate necessary for complete oxidation of the acid was investigated. But it was found that the salt acts as a positive catalyst at first, then as an inhibitor, its negative action appearing when the quantity of catalyst is increased. Manganous sulphate was therefore discarded for, in titration, the salt is being formed continuously, and this tends increasingly to inhibit the oxidation. The negative catalytic action of manganese sulphate may be explained by the formation of an intermediate unstable compound of manganic sulphate and dihydroxytartaric acid which increases as the quantity of manganous sulphate increases.[19]

As would be expected the effect of temperature is to decrease the time of decolorisation, that is, the time of decomposition.

Two sets only are recorded out of a number of series of observations. In each of the following series 10 ml. 0·1 N. (approx.) dihydroxytartaric acid was used which was just sufficient to decolourise the 8·5 ml. 0·1 N. potassium permanganate added. Variable quantities of a solution of $MnSO_4 4H_2O$ (1·6 N. approx.) acidified with dilute sulphuric acid to stabilise it, was added to the reacting mixture which had been acidified with 10 ml. sulphuric acid (5·N.) and 10 ml. phosphoric acid (6·5 N.). The reaction volume was finally made up to 150 ml. with water and observations of time taken.

Table I.

Ml. $MnSO_4$ solution taken.	Time to decolourise in minutes.	Temperature of bath.
0	69·5	6·5
0·25	48	6·5
2	60	6·5
3	68	6·5
0	52	14
0·25	27	14
2	42	14
3	49	14

[19] Compare "Inorganic and Theoretical Chemistry," Mellor, Vol. XII., p. 325.

Catalytic Activity of Vanadium Pentoxide.—It is well known that vanadium pentoxide accelerates the oxidation of organic compounds.[20] It was found that anomalous results were obtained in the rate of oxidation using a suspension of vanadium pentoxide in water acidified with sulphuric acid. This is probably due to the formation of hydrated vanadium pentoxide. Acidified ammonium meta-vanadate gave slightly better, but still anomalous results; particularly was this the case after keeping the solution for some hours. The difficulty regarding the variable nature of this catalyst can be overcome by preparing a fresh solution immediately before use.

In the following experiments the catalyst used was of a variable concentration of ammonium meta-vanadate acidified just before use with a few drops of dilute sulphuric acid. Each experiment was carried out with 10 ml. 0·1 N. (approx.) dihydroxytartaric acid, 7·5 ml. 0·1 N. potassium permanganate (not sufficient for complete oxidation of the acid) acidified with sulphuric and phosphoric acids and made up to the reaction volume as in the previous manganous sulphate series.

TABLE II.

Ml. of catalyst used.	Strength of catalyst solution or suspension gm. of ammon. meta-vanadate in 100 ml.	Time to decolourise in minutes.	Temp. °C.
0	0	70	10
1	2	15½	10
3	2	10¼	10
5	2	5½	10
10	2	3½	10
15	2	2¾	10
0	0	67	12·5
3	0·05	54	12·5
5	0·05	48	12·5
10	0·05	30	12·5

From the above results it is seen: (*a*) vanadium pentoxide acts catalytically; (*b*) the rate of oxidation increases with increasing quantity of catalyst; (*c*) even a small amount of catalyst reduces the time of decolorisation to 30 minutes (less than half time); (*d*) the initial positive catalytic action of manganese sulphate is small compared with this very reactive catalyst.

Action of Vanadium on Potassium Permanganate.—Rutter and Lindenbaum[21] state that vanadium has a slow action on permanganate. This was found to be the case, and an error, though small, is introduced and can be corrected for if desired. The

[20] Naumann, Moeser and Lindenbaum, *J. prakt. Chem.*, 1907 (11), 75, 146; cf. "Inorganic Chemistry," Vol. VI. (III.), Marks (J. Newton Friend), p. 34.

[21] *Zeit. Anorg. Chem.*, 1907 **52**, 368; *J. Pr. Chem.*, 1907 (11), **75**, 146.

following experiments were carried out under identical conditions. After mixing the reagents the reaction volume was made up as before to 150 ml., the solution put in a water bath for 20 minutes at 14°, then heated to 52° and the excess of permanganate titrated by means of standard oxalic acid. The catalyst employed was 0·05 per cent. solution of ammonium metavanadate slightly acidified with dilute sulphuric acid.

TABLE III.

Ml. of catalyst.	Ml. H_2SO_4 (5N).	Ml. H_3PO_4 (6·5N).	Ml. 0·1 N $KMnO_4$	Ml. standard oxalic acid used.
0	20	20	15	5·95
3	20	20	15	5·80
5	20	20	15	5·65
10	20	20	15	5·40

In each case 10 ml. 0·1 N. (approx.) of dihydroxytartaric acid were used. A fresh solution of dihydroxytartaric acid was prepared, and the following were carried out under identical conditions as those in Table III. using the same quantities of acids, permanganate, etc., in the same reaction volume but for 1 ml. of catalyst, time of standing being 20 minutes at 14° C.

TABLE IV.

Ml. catalyst 0·05 per cent.	Ml. standard oxalic acid required.
0	2·10
1	2·04
1	2·03
1	2·03

Thus vanadium has a definite action on permanganate, but using quantities as 1–3 ml. catalyst solution the error introduced is small and can be neglected. The object of using a catalyst is to increase the rate of oxidation at a low temperature so as to prevent any profound abnormal change taking place in the constitution of the acid, and thus being able to carry out a theoretical quantitative normal estimation. The quantity of catalyst used in all subsequent experiments is 2·3 ml. of a 0·05 per cent. ($[NH_4]VO_3$) acidified solution. The vanadium pentoxide is in colloidal solution (solubility of V_2O_5 is 0·125 per cent).

No correction has been applied for the action of vanadium on permanganate. Ammonium molybdate, uranium acetate and ceric sulphate were investigated for catalytic action. They all possess a certain catalytic activity, molybdenium being fairly good and uranium poor. Ceric sulphate being a strong oxidising agent acts on the acid and cannot be used for the error introduced would be large.

Method of Titration with Potassium Permanganate.

The method adopted for titration of the acid by means of potassium permanganate is similar to that used for the sodium salt. An excess of potassium permanganate is added to the dihydroxytartaric acid solution in presence of dilute sulphuric and phosphoric acids, together with the vanadium catalyst. The volume is made up to 350 ml. with distilled water, then allowed to stand 20 minutes at room temperature, and the permanganate is back titrated with standard oxalic acid at a commencing temperature of 52–53° C. and a temperature of 48–49° C. at the end point of the titration (if carried out at a reasonable speed).

The presence of phosphoric acid is necessary, it gives a distinctive initial purple colour to the permanganate, increases the sharpness of end point on back titration and prevents considerably the formation of hydrated manganese dioxide.[22].

Estimation of Sodium by Potassium Dihydroxytartrate.

Solutions of sodium chloride of varying strengths were prepared by direct weighing and their concentrations were checked by titration with silver nitrate. The solutions employed were as follows.

Table V.

Solution.	Grams NaCl per litre.	Equivalent grams of Na per litre.	Grams of Na per 5 ml. employed in experiments.
1	4·9968	1·9645	0·0098
2	9·9936	3·9291	0·01965
3	19·9598	7·8472	0·03924
4	30·1333	11·8475	0·05924
5	40·1087	15·7692	0·07885

As suggested by Fenton, dihydroxytartaric acid was neutralised by potassium carbonate solution to form the precipitating reagent, and in each experiment 1 gram of the acid, that is, a large excess, was employed. The solubility of potassium dihydroxytartrate is 2·7 per cent. at 0°, the weight of potassium salt corresponding to 1 gram of acid is 1·42 grams, which is soluble in 52·6 ml. of water at 0°, and therefore 50 ml. is about the minimum quantity (at 5°) of the total solution for precipitating sodium as sodium dihydroxytartrate in order to avoid precipitation and heavy occlusion of the potassium salt.

Experimental Details.—A large water bath kept at 5° C. (certain experiments 10°) was employed, all solutions and wash water being kept in it ready for use. 5 ml. dihydroxytartaric acid solution (containing 1 gram of acid) was mixed with 35 ml. ice

[22] Cf. the Zimmermann-Reinhardt method of titration of ferrous salts in hydrochloric acid solution.

cold water, 5 ml. potassium carbonate solution (containing 153·9 gram/litre, the quantity of potassium carbonate being calculated from the percentage purity of the dihydroxytartaric acid) and 5 ml. sodium chloride solution in a small (60–70 ml.) beaker. This volume of 50 ml. was kept constant throughout all experiments. The beaker was kept in the water bath for the requisite time. The precipitate was filtered off by slightly reduced pressure on to a 2·3 cm. diameter perforated disc covered with two No. 42 Whatman filter papers of very slightly larger diameter. The precipitate and filter papers* were washed with 10–13 ml. ice-cold distilled water, transferred to a conical flask in which there was excess of potassium permanganate acidified with sulphuric and phosphoric acids and 2 ml. of freshly prepared ammonium meta-vanadate solution (0·05 per cent.) acidified with a few drops of dilute sulphuric acid. The volume was made up to 350 ml., allowed to stand 20 minutes, heated to 52° C., and the excess of potassium permanganate titrated with standard oxalic acid solution. The following table gives the necessary data with respect to potassium permanganate, sulphuric and phosphoric acids necessary to employ and which correspond to the 5 solutions in Table V.

TABLE VI.

Solution.	Ml. potassium permanganate used.	Ml. H_2SO_4 5 N.	Ml. H_3PO_4 6·5 N.
1	15	50	50
2	25	50	50
3	40	50	50
4	60	75	75
5	75	100	100

Absence of Sodium in Reagents Used.—The A.R. K_2CO_3 was tested for sodium (simultaneously with dihydroxytartaric acid) by neutralising with dihydroxytartaric acid in solution of maximum concentration, by allowing to stand at 0° for 8 hours, and no precipitation occurred. In later experiments A.R. ammonium chloride and A.R. magnesium sulphate were employed, and were tested as above with potassium dihydroxytartrate without any sign of precipitation.

Correction for Solubility of the Sodium Salt.—The solubility of the sodium salt at 5° and 10° is 0·042 and 0·053 per cent. respectively; these values correspond to 0·0085 and 0·0108 per cent. of sodium respectively. Correction was made at the working temperature for the total volume in which precipitation took place together with the volume of wash water used.

* The error introduced by transferring the filter papers to the oxidising media is less than 0·05 ml. of 0·1 N potassium permanganate.

Experimental Results.

Table VII.

	Solution 1.		Solution 2.			
Time of standing prior to filtration (hrs.)	5	18½	1½	5½	19½	18
Temp. of filtration	5	5	5	5	5	10
Ml. of wash water	10	10	10	10	10	10
Ml. of $KMnO_4$ solution* added	15	15	25	25	25	25
Ml. of 0·10429 N oxalic acid to titrate the excess permanganate	12·90	11·79	24·20	20·75	11·80	16·74
Ml. of 0·10429 N oxalic acid equiv. to Na salt estimated	7·12	8·22	11·15	12·60	21·55	16·61
Gms. of Na present	0·0098	0·0098	0·0196	0·0196	0·0196	0·0196
Gms. of Na found	0·0057	0·0066	0·0089	0·0101	0·0172	0·0133
Error due to solubility and occlusion + non-precipitation	−0·0041	−0·0032	−0·0107	−0·0095	−0·0024	−0·0063
Percentage error due to solubility and occlusion + non-precipitation	−41·8	−32·5	−54·5	−48·5	−12·2	−32·1
Positive correction for solubility of sodium salt	0·0051	0·0051	0·0051	0·0051	0·0051	0·0065
Grams of Na found corrected for solubility	0·0108	0·0117	0·0140	0·0152	0·0223	0·0198
Error due to occlusion + non-precipitation	+0·0010	+0·0019	−0·0056	−0·0044	+0·0027	+0·0002
Percentage error due to occlusion + non-precipitation	+10·2	+19·4	−28·6	−22·5	+13·8	+1·0

* 25 ml. $KMnO_4$ = 33·35 ml. of oxalic acid solution.

The following points are of interest with regard to Table VII., solution 1: (1) the error due to solubility and occlusion + non-precipitation is large compared to the weight of sodium present and decreases with increase of time of standing; (2) occlusion + non-precipitation increases with time as would be expected, for the non-precipitation would be smaller, *i.e.*, quantity of sodium estimated would be greater with increase of time of standing; (3) the estimation at this dilution is unsatisfactory for generally the estimation is subject to very large percentage errors.

Solution 2.—With regard to the first three columns, the same comments are applicable in the main, although at this concentration, after standing 19½ hours, a comparatively better estimation of sodium has been attained; but, again, at this concentration the estimation is not satisfactory—the error due to solubility and occlusion + non-precipitation being very high. The influence of temperature is shown in the last column, although the error due to solubility and occlusion + non-precipitation is high, almost 33 per cent. and error due to occlusion + non-precipitation has decreased to 1 per cent., the counterbalance is such that the estimation after applying a 33 per cent. solubility correction is approximately correct. The correcting factors are too large here, and thus sodium cannot be estimated accurately at this concentration.

TABLE VIII.

	Solution 3				
Time of standing prior to filtration (hrs.)	1½	3½	5	20	26
Temp. of filtration	5	5	5	5	10
Ml. of wash water	13	10	10	10	12
Ml. of $KMnO_4$ solution added	40	40	40	40	40
Ml. of 0·10429 N oxalic acid to titrate the excess permanganate	8·17	7·25	6·50	6·05	11·31
Ml. of 0·10429 N oxalic acid equivalent to Na salt estimated	45·19	46·11	46·86	47·31	42·05
Gms. of Na present	0·0392	0·0392	0·0392	0·0392	0·0392
Gms. of Na found	0·0361	0·0368	0·0375	0·0378	0·0337
Error due to solubility and occlusion + non-precipitation	−0·0031	−0·0024	−0·0017	−0·0012	−0·0055
Percentage error due to solubility and occlusion + non-precipitation	−7·90	−5·85	−4·32	−3·55	−14·00
Positive correction for solubility of sodium salt	0·0053	0·0051	0·0051	0·0051	0·0067
Grams of sodium found corrected for solubility	0·0414	0·0419	0·0426	0·0429	0·0404
Error due to occlusion + non-precipitation	+0·0022	+0·0027	+0·0034	+0·0037	+0·0012
Percentage error due to occlusion + non-precipitation	+5·6	+6·9	+8·6	+9·4	+3·0

Table VIII. deals with the analysis of solution 3 carried out at temperature 5°, except the last column which was at 10°. Note the following: (1) error due to solubility and occlusion + non-precipitation, as before, decreases with increase of time of standing; (2) error due to occlusion + non-precipitation increases slowly with increase of time of standing; (3) the temperature factor has a similar effect as in the previous case (Table VII., Solution 2); (4) when the time of standing is 3½ to 5 hours results obtained appear satisfactory, but errors expressed in percentages are too

TABLE IX.

	Solution 4.				Solution 5.		
Time of standing prior to filtration (hrs.)	3½	5½	20½	21½	3	4½	21
Temp. of filtration	5	5	5	10	5	5	5
Ml. of wash water	13	13	10	10	13	13	10
Ml. of $KMnO_4$ solution added	60	60	60	60	75	75	75
Ml. of 0·10429 N oxalic acid to titrate the excess permanganate	16·15	11·55	8·37	13·00	9·73	8·84	3·67
Ml. of 0·10429 oxalic acid equivalent to Na salt estimated	63·89	68·49	71·67	67·04	90·32	91·21	96·38
Gms. of Na present	0·0592	0·0592	0·0592	0·0592	0·0788	0·0788	0·0788
Gms. of Na found	0·0511	0·0548	0·0573	0·0536	0·0722	0·0729	0·0771
Error due to solubility and occlusion + non-precipitation	−0·0081	−0·0044	−0·0019	−0·0056	−0·0066	−0·0059	−0·0017
Percentage error due to solubility and occlusion + non-precipitation	−13·61	−7·4	−3·2	−9·4	−8·50	−7·60	−2·18
Positive correction for solubility of sodium salt	0·0053	0·0053	0·0051	0·0064	0·0053	0·0053	0·0051
Grams of sodium found corrected for solubility	0·0564	0·0601	0·0624	0·0600	0·0775	0·0782	0·0822
Error due to occlusion + non-precipitation	−0·0028	+0·0009	+0·0032	+0·0008	−0·0013	−0·0006	+0·0034
Percentage error due to occlusion + non-precipitation	−4·7	+1·5	+5·4	+1·35	−1·65	−0·76	+4·3

high for the weight of sodium taken is comparatively small. This solution is again not sufficiently concentrated to give a good estimation.

Solutions 4 *and* 5.—From inspection of the data which is self explanatory, these solutions are sufficiently concentrated for satisfactory estimation of sodium, but the time of standing should not exceed 4½ to 5 hours, otherwise error due to occlusion + non-precipitation will increase. These two factors tend to counterbalance each other. All the above experiments were carried out in duplicate, the difference in titration being of the order of 0·1 to 0·6 ml. of standard oxalic acid (1 ml. of oxalic acid 0·10429 N. is equivalent to 0·00079 gram sodium).

Ideal Conditions for Estimation of Sodium.—Reasonably accurate results are to be expected when concentration of sodium lies between 7–11 grams (Na) per litre. In order to obtain almost complete precipitation with minimum occlusion counterbalancing the non-precipitation the time of standing should be 4½ to 5 hours. Filtration temperature should be as near to 5° as possible, and at any rate not higher, otherwise error due to solubility of the sodium salt would be greater. In precipitating the sodium dihydroxytartrate with the potassium salt, the latter solution is added to the former drop by drop with stirring.

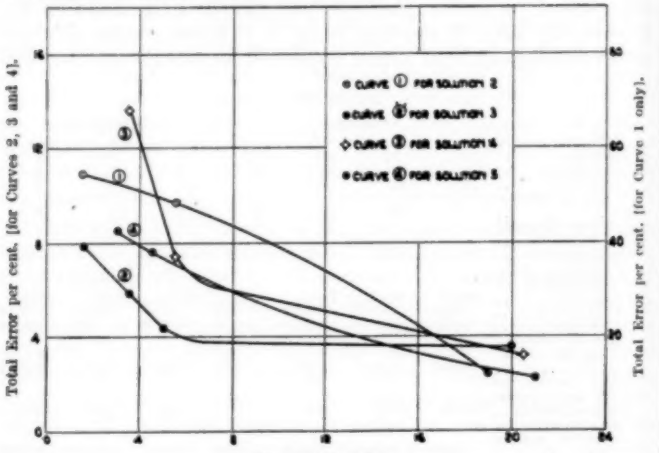
Total Error per cent. [for Curves 2, 3 and 4].
Total Error per cent. [for Curve 1 only].
Hours of Standing.
CURVE ① FOR SOLUTION 2
CURVE ② FOR SOLUTION 3
CURVE ③ FOR SOLUTION 4
CURVE ④ FOR SOLUTION 5

DIAGRAM I.

Diagram I. represents the total percentage error (per cent. error due to solubility and occlusion + non-precipitation) obtained

from the tables which is negative plotted against time of standing. The errors as shown in curve 1 are becoming comparable with the quantity of sodium estimated. In curve 2 the solubility correction is large compared with the weight of sodium present. These two concentrations are not to be recommended for analysis for the

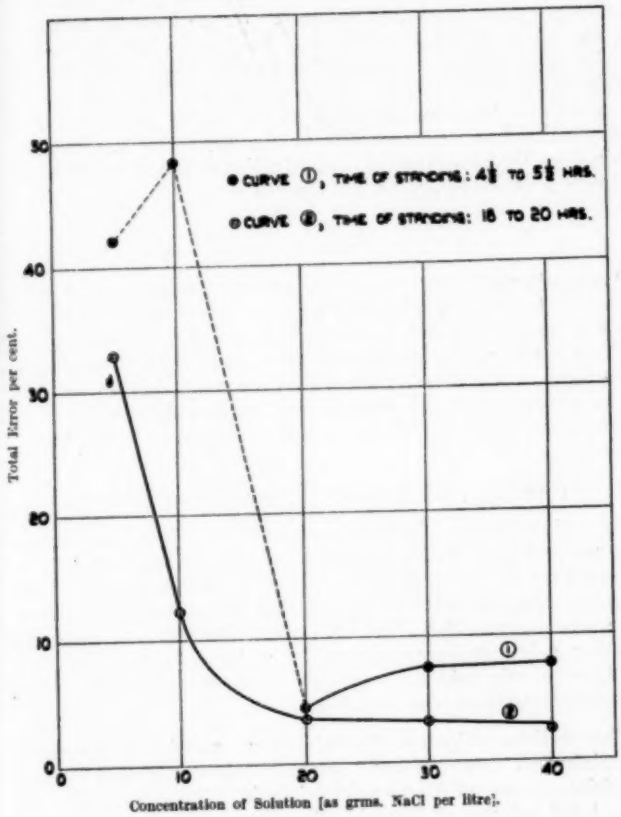

DIAGRAM II.

curves are displaced with respect to curves 3 and 4, which bear similar relationships to each other. Generally the following remarks may be made : (1) the total error falls as the time of standing increases ; (2) the rate of decrease in the error is much

more marked in lower than in higher concentrations; (3) after the time of standing has reached the neighbourhood of 5 hours the total error is practically constant and is nearly the same for concentrations between 8 and 16 grams approx. of Na per litre (20–40 grams approx. NaCl per litre).

Diagram II. represents total error plotted against the concentration per litre of sodium chloride. Curve 1 shows irregularity for the time of standing has not been sufficient for complete precipitation at low concentration but at higher concentrations regularity is observed. Curve 2 shows how rapidly the error decreases as the concentration is increased, and proves that precipitation has been complete or almost complete. The curves again show that the range of concentration required for satisfactory estimation is 20–40 grams NaCl per litre.

Use of Ceric Sulphate for Titration.

Preparation of Ceric Sulphate Solution.—Purified cerous oxalate converted to ceric oxide by heating in a muffle at 600° C. in a crucible for 8 hours was cooled, mixed with concentrated sulphuric acid to form a stiff paste, and heated on a water bath with occasional stirring for 16–20 hours. The cooled mass was diluted with water to the required strength and filtered. Ceric sulphate solution can be titrated against oxalic acid solution according to the following equation :—

$$(COOH)_2+2Ce(SO_4)_2=Ce_2(SO_4)_3+H_2SO_4+2CO_2.$$

Since ceric sulphate solution can replace potassium permanganate, the precipitated sodium dihydroxytartrate was subjected to exactly the same procedure as in the case of estimation by potassium permanganate, with the exception that the catalyst was found to be unnecessary. Phosphoric acid was omitted for it interacts forming gelatinous ceric phosphate; instead, the quantity of dilute sulphuric acid as employed when estimating by the permanganate method was doubled.

The sodium dihydroxytartrate was transferred to a flask containing an excess of ceric sulphate solution (about 0·1N), the requisite amount of dilute sulphuric acid (5N) and distilled water to a total volume of 350 ml. The excess of ceric sulphate was titrated with standard oxalic acid. The ceric sulphate solution was standardised by oxalic acid under conditions identical with the above. Table X. shows two series of experiments which were carried out in duplicate. The results are in reasonably good agreement with those obtained by the permanganate method.

TABLE X.

Time of standing prior to filtration (hrs.)	5	5½
Temp. of filtration	5	5
Ml. of wash water	10	10
Ml. of $Ce(SO_4)_2$* solution added	25	75
Ml. of 0·10429 N oxalic acid to titrate the excess ceric salt	16·57	20·60
Ml. of 0·10429 N oxalic acid equivalent to Na salt estimated	6·23	47·80
Gms. of Na present	0·0098	0·0392
Gms. of Na found	0·0050	0·0378
Gms. of Na found by $KMnO_4$..	0·0057	0·0375
Error due to solubility and occlusion + non-precipitation	—0·0048	—0·0014
Percentage error due to solubility and occlusion + non-precipitation	—48·9	—3·5
Positive correction for solubility of sodium salt ..	0·0051	0·0051
Grams of sodium found corrected for solubility ..	0·0101	0·0429
Error due to occlusion + non-precipitation ..	+0·0003	+0·0037
Percentage error due to occlusion + non-precipitation	+3·0	+9·4

* 25 ml. of $Ce(SO_4)_2$ solution is equivalent to 22·8 ml. of 0·10429 N oxalic acid solution.

These results bear out what has already been discussed concerning the previous tables of results, namely, that both solutions are not sufficiently concentrated for accurate work. It should be mentioned that any error in the titration and variation in the normal oxidation of the acid would appear as an error in occlusion + non-precipitation.

INFLUENCE OF AMMONIUM CHLORIDE ON THE PRECIPITATION OF THE SODIUM SALT.

The influence is to increase the solubility of sodium dihydroxytartrate and cause low results. This is indicated in Table XI. and also on Diagram III., as the quantity of ammonium chloride

TABLE XI.

Grams of NH_4Cl present.	Ml. of permanganate added.	Ml. oxalic acid required to titrate excess permanganate.*	Ml. oxalic acid equivalent to sodium salt.	Grams of sodium found.
0·125 ..	60 ..	8·78 ..	68·80 ..	0·0550
0·250 ..	60 ..	10·10 ..	67·47 ..	0·0539
0·750 ..	60 ..	11·96 ..	65·61 ..	0·0525
1·500 ..	60 ..	13·53 ..	64·04 ..	0·0512
2·250 ..	60 ..	14·64 ..	62·93 ..	0·0503

Grams of sodium present 0·0592. Time of standing was 5 hours in all cases.
* 25 ml. permanganate = 32·32 ml. oxalic acid 0·10419 N.

increases so the weight of sodium found decreases. The method of analysis was the same as before, a solution containing the desired quantity of ammonium chloride was added in each experiment, the reaction volume being always 50 ml. Ammonium chloride

in large quantity gives a pink-brown colour with potassium dihydroxytartrate. The following data can be employed for correction for solubility of sodium dihydroxytartrate when ammonium chloride is present, the amount of which in solution should be known.

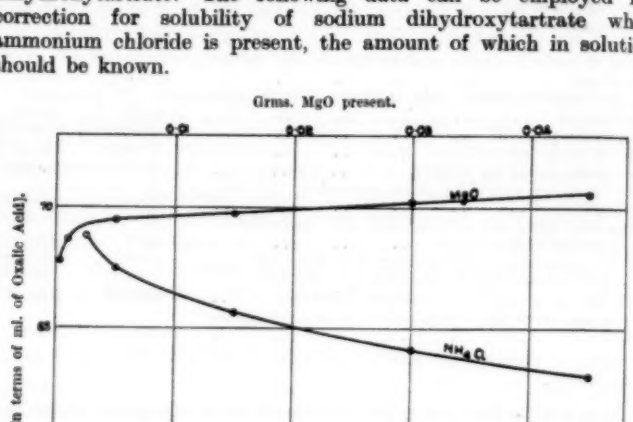

DIAGRAM III.

INFLUENCE OF MAGNESIUM SULPHATE ON THE PRECIPITATION.

It is probable that magnesium itself is precipitated as magnesium dihydroxytartrate to a small extent, which contaminates the sodium salt, causing slightly high results. The effect is shown in Table XII. and Diagram III. The precipitation is tending apparently to reach a maximum.

TABLE XII.

Grams of MgO present.	Ml. of permanganate added.	Ml. oxalic acid to titrate excess permanganate.*	Ml. oxalic acid equivalent to sodium salt.	Grams Na found
0·00025	60	11·68	67·76	0·0542
0·001	60	10·80	68·64	0·0549
0·005	60	9·99	69·45	0·0555
0·015	60	9·75	69·69	0·0557
0·030	60	9·25	70·19	0·0562
0·045	60	8·92	70·52	0·0564

Time of standing was 5 hours in all cases. Grams of sodium present 0·0592.

* 25 ml. $KMnO_4$ = 79·44 ml. oxalic acid 0·10419 N.

The method of analysis was identical to that employed in the case of estimation of sodium alone. The desired weight of magnesium sulphate was added in solution, the reacting volume being kept constant at 50 ml. Results have been tabulated in terms of grams of MgO.

When an attempt is made to estimate sodium by this method in the presence of both ammonium and magnesium salts, a very considerable solvent action is noticeable which causes extremely low results; thus, a correction for ammonium salts cannot be applied in the presence of magnesium salts. This may be due to the formation of a magnesium ammonium compound,[23] which has a different solvent action on sodium dihydroxytartrate to either of the components of the double magnesium ammonium salt, namely, magnesium sulphate and ammonium chloride.

Summary.

1. Potassium dihydroxytartrate is a suitable reagent at 5° C. for precipitating sodium as the sodium salt owing to the low solubility of the latter.

2. Vanadium pentoxide is an excellent catalyst for promoting the normal oxidation of dihydroxytartaric acid or its sodium salt. This catalyst should be freshly prepared by acidifying a 0·05 per cent. solution of ammonium metavanadate. Further, its action on permanganate is small and can be neglected.

3. The method of estimation and titration adopted is to use a definite reaction precipitation volume and a definite titration volume, correct and normal estimation being ensured by oxidation at a low temperature in the presence of an excess of permanganate, definite quantities of sulphuric and phosphoric acids and a catalyst.

4. In all the results a negative error was obtained, which, when corrected for the solubility of the sodium salt at 5°, in most cases gave a positive error. The higher the concentration the smaller was this error.

5. This research shows that sodium is best estimated in concentration of about 8–16 grams Na (20–40 grams NaCl) per litre.

6. Ceric sulphate can replace permanganate as an oxidising agent for the estimation. The objections which can be raised against its use are: ceric sulphate solution takes at least two days to prepare, and cerous oxalate is not so easily procurable as potassium permanganate.

[23] Mellor, "Inorganic and Theoretical Chemistry," Vol. IV., p. 306.

7. The presence of ammonium salts cause markedly low results, and, if their concentration is not known, removal by evaporation and treatment of the residual liquor by nitric acid is advisable.

8. Magnesium if present causes a slightly high result, but it is not appreciably high. The combined effect of magnesium and ammonium salts is abnormal, giving very low results.

The authors are greatly indebted to Professor A. W. Nash for the facilities which he has provided for the carrying out of this research.

DEPARTMENT OF OIL ENGINEERING AND REFINING,
UNIVERSITY OF BIRMINGHAM.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE TWENTY-SEVENTH GENERAL MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on Wednesday, January 27th, 1932, Mr. A. F. DABELL, Branch Chairman, in the Chair.

The Chairman, in opening the meeting, said that the Committee had decided that a report of an open discussion by the Rumanian Branch upon the "Behaviour of Restricted Wells,"[1] which was initiated by Mr. G. Elias, should be read.

In the absence of the Hon. Secretary, **Mr. C. E. Capito** then read those parts of the paper essential to discussion.

The Chairman, in opening the discussion, said that in effect Mr. Elias declares that a curve drawn through the potential peaks would approximate the normal decline curve, which being accepted, then do the areas between the peaks on the diagram represent loss or deferred production, and that in his opinion it is mostly, if not totally, lost. He then asks where has it gone, and tenders the possible explanation that thief sands might be responsible.

Like the origin of oil, the matter is of far-reaching interest, in that knowledge of the matter should assist in the problem of better production methods.

So far as he knew there is no more evidence of thief sands in Rumania than elsewhere; therefore, this remote contingency should receive consideration only as a final resort.

Holding that ultimate recovery is dependent upon porosity, he suggested that when migration of oil toward a well is arrested by, *e.g.*, abnormal restriction, the lighter fractions of that oil in the immediate vicinity of the well will be released, raising the viscosity of the remaining oil and creating a form of barrier in the sand around that well.

The same would apply to abnormal release.

Under these conditions migration from distant radial points upon which recovery is dependent, will be arrested.

The result, therefore, under the conditions described in Rumania would be that the oil is not lost, it remains in the sand, and the abnormally restricted wells have a reduced area of drainage.

The experience in Rumania is not new, but it has not previously been so clearly recorded.

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[1] *J. Inst. Petr. Techn.*, 1931, 17, 611–620.

For instance, an article by Mills[2] reads :—

"Before curtailment was actually tried at Ventura, it had been contended that wells would spring back immediately after a shut-in period and that production would be much higher for several months after proration was lifted. Operators in the field agreed to 'cut back' their wells for 90 days. Instead, the wells remained partially shut-in for 120 days. When the ban was lifted and wells opened up, the much vaunted jump in production did not occur. Production started off at about the same rate it would have been had no conservation program been carried out. Theoretically, production from each well was expected to jump considerably above what would have been uninterrupted line of production. The wells had been shut-in, oil had been saved and gas production was much smaller as well. It seemed that upon reopening, all of the old energy, plus the stored energy of 120 days, would give a sharp increase to production. Only in a few wells did the increase meet expectations, however.

"The question of whether the oil 'lost' through curtailment would be recovered at a later date immediately arose.

"The old theory that the best time to get oil is when the gas pressure is highest, seems to apply to the Ventura Field." But is is to be noted that no explanation is offered.

Again, Ray E. Kellar, under the heading of "The Significance of Gas Oil Ratios,"[3] declares that :—

"The practice of applying back pressure to producing wells with a view to deferring production has been advocated. This has not proven feasible in connection with these properties. In one instance in the Seminole field, a well was connected in such a manner that it could be produced through either the tubing or the annular space between the tubing and the casing. A recovery of 2976 barrels of oil per day was secured when the well was produced through the annular space, while the best production obtainable through the tubing was only 276 barrels per day. These data were secured in connection with the operation of producing wells during proration periods. Unquestionably, these figures represent a prohibitive penalty in 'deferred production' through the application of back pressure on the producing sand. There is already some evidence at hand, secured during proration periods, which would indicate that a part of this deferred production at least may not be recovered in the later stages of the production life of the field."

[2] *Oil Weekly*, 1927.
[3] *Oil Weekly*, 23.5.30.

In support of the contention advanced, he would again refer to an article by that very practical writer upon oilfield development, Pennington, who declares that :—

"the influence zone of wells is proportional to the freedom of flow through the porous container-sand ; and 'if the degree of porosity be reduced the flow is restricted by capillarity and friction and with heavy oil, viscosity.'"

Other factors being equal, the volume of oil and gas produced by a well depends upon the differential pressure between the well and oil and gas surrounding the well.

C. V. Millikan has written as follows :—

"In a well in which the pressure differential between the sand and the well is constant there is a steady rate of movement of the oil through the sand. If the gas flow is checked a large number of pore spaces which had been kept open by the moving gas will close because of capillary attraction."

It is to be learned, therefore, that excessive restriction is wasteful, and where restriction is necessary it would be better obtained by restricted drilling, and, incidentally, it is to be hoped that the powers that control our destiny will bear this in mind.

Mr. Albert Millar said that the discussion of Mr. Elias' paper on the effects of restricted production and the behaviour of restricted wells opened up a very wide field for study and investigation.

The only chance for restricted production (proration) proving completely successful is where the whole oil-bearing structure is under the control of a single company, and then only if the production engineers of that company have made a close and very careful study of all conditions appertaining to the field.

It can be successfully applied, however, where the structure is governed by three or four major concerns which have been co-operating and pooling their knowledge in order to achieve the best results for each undertaking, which incidentally means the most rational exploitation of the structure as a whole.

Such co-operation would hardly be possible in Rumania and many other fields where similar conditions exist. With very few exceptions the producing areas are divided into comparatively small plots. Even under the best conditions offset wells will be drilled in close proximity on possibly two or three sides of any one plot. It is quite conceivable that thirty or more companies or individual undertakings may be interested in any one structure, and it is highly probable that each of these in turn will have several plots scattered over this same area. A number of these

sub-divided plots will only afford room for three or four closely-spaced wells.

To attempt restriction of production under such conditions is bound to cause trouble and result in failure. Little or no co-operation exists between those interested and there is certainly no pooling of information, unity of purpose of applied standardised methods. As is usually the case where decentralisation exists, each unit operating thinks only for itself and how it can produce more oil than its neighbour, whom it generally views with suspicion.

To enforce restriction under such conditions would be at the best a most difficult proposition and could certainly never have a 100 per cent. chance of its being a success.

If restriction is to be put into force it is of primary importance that the field in question be considered as one complete unit and not as a multiplicity of small units. Neither can it be left to the goodwill of individual operators to restrict production as they may consider best, from that particular section of the structure in which they are interested.

There is only one way that can lead to complete success where the interests are divided, and that is to put the field as one complete unit under the absolute control of a few specialist petroleum engineers, who, after carefully studying all conditions, would carry out a programme of restriction that would be effectual, and at the same time not prove detrimental to the structure considered as a unit.

In reviewing the discussion of Mr. Elias' paper he found very little of that class of data which is most essential to formulate a theory which would account for the erratic behaviour of the wells in question. To achieve this it would be necessary to know :—

1. Diameter of borehole.
2. Depth of well.
3. Size of flow tubing and depth at which it is set.
4. Thickness of producing sand or sands.
5. Texture of such sands.
6. Total volume of oil and gas already produced by the wells in question.
7. The same information regarding adjacent wells.
8. Situation of wells in the immediate vicinity.
9. Position of wells under discussion and that of neighbouring wells on the structure.

Well B.—From the general behaviour of this well it would seem to be a perfect specimen of hydraulic control. As this well was located in a newly-developed area at the time, it suffered little or nothing by being restricted.

There is nothing abnormal in the way the casing pressures fluctuated and he did not understand what Mr. Elias meant when he referred to "peculiar condition."

There is one point, and that is the very abrupt change of bean sizes, as, for instance, 12 to 5 mm.; 17 to 4 mm.; 28 to 7 mm.; 15 to 5 mm.; etc.

Anyone familiar with the handling of very sensitive wells knows the trouble that is likely to occur as a result of changing the sizes of beans too suddenly.

The behaviour of these wells, situated on or close to the top of the structure, which were beaned back or closed in, is what was to be expected and is quite normal. It is common and good practice to shut in wells so situated, wherever possible. This is done is order to conserve the gas and to thereby utilise it to force the oil to those wells lower down the structure.

Mr. Crooks, in discussing well No. 4 Cura Ochnitei, does not mention under what conditions the other wells surrounding this well were producing, during the period No. 4 was shut in for technical reasons. In all probability the other wells were the gainers thereby.

The same remarks apply to well No. R.A. 165. What happened to the neighbouring wells during the time that this one was shut in ?

He could not agree with Mr. Crooks' statement that decrease in size of bean means loss of ultimate production. It is necessary to bean back a well in order to conserve the gas energy in the sand, and the rapid expansion of the gas can only take place where there is a corresponding movement of oil and gas to the wells.

Mr. Crooks mentioned No. 13 Boldesti, where the well had to be closed in because an adjoining well "blew in." This can hardly be taken as a fair example. It would be very interesting to learn what effect the "wild" well had on No. 13 Boldesti, and others in the vicinity.

Then again, No. 15 Boldesti is referred to. It appears that this well was producing normally until it was alternatively—shut in, opened up, flow bean altered, again shut in, etc., etc. The best one can say is that this is exceptionally severe, and certainly not normal treatment, and is not to be taken as a criterion of the possible results to be gained, had proper control been exercised.

Mr. Elias' paper provides a most excellent example of the detrimental effects sustained by partial control. He did not think that the paper in any way makes out a case against restriction or beaning back of wells; to the contrary, it is rather

a glaring example of uncontrolled control, and proves a strong argument in favour of unit control of oilfields.

Mr. G. H. Scott said that as a protagonist of the principles of gas conservation he felt that the discussion just heard does nothing to disprove these principles. A restriction of flow made for the purpose of increasing lift efficiency is a very different matter to a restriction made solely for reduction of production rates.

It is obvious that for any one set of conditions in a flowing well there must be an optimum rate of flow which gives maximum efficiency. Any restriction of flow below this optimum rate will result in a lowered efficiency with a consequent increase in the gas/oil ratio. This condition must have existed in several of the wells quoted where beaning back was attended by sharp increases in the gas/oil ratios. If one considers the fluid produced by a well as a mixture of oil and gas, with a very great difference in gravity between the two components, there is a certain low limit of velocity below which no oil will be raised by the ascending gas, in which case the gas/oil ratio will be infinity. Similarly, with wells of high potential production rates, if rates of flow are permitted which are in excess of the critical velocity of the flow string, turbulence will be set up and at best the flow will be characterised by periods of heading. This critical velocity will diminish with decreases in size of the flow string.

It is unfortunate that Mr. Elias forbore to mention the nature of the peculiar conditions which renders it necessary to discount the casing-head pressures in the first well quoted by him. It is indeed extraordinary to find that, with one or two exceptions only, these are below the observed figures of tubing-head pressure.

Further, with the extraordinary units of measure quoted, it is impossible to state whether the gas/oil ratios are a true ratio of cubic feet of gas to a cubic foot of oil, or the more usual value of cubic feet of gas to one barrel of oil. In the latter case it can be stated almost definitely that the flow conditions are due to a natural water drive and not to a gas pressure head. Assuming a reservoir pressure of about 750 lb./sq. in. gauge pressure, the amount of gas dissolved in one barrel of oil would be about 140 cu. ft., so that the flow efficiency would be in excess of 100 per cent. This is impossible if flow is due to gas energy alone. The constancy of gas/oil ratios with decrease in choke sizes also indicates that hydraulic head conditions of flow exist there.

In the third instance, quoted as Well "A," no mention is made of the proximity of neighbouring wells and their behaviour during

the periods of restriction. If producing sands are persistent, and if back pressure is held on one well only of a group, there will be a tendency for increases in the production rates of neighbouring wells. If the restricted well is situated high up on structure the increased production of wells down structure might very well cause the gas/oil level to sink so that only gas would be produced. There is evidence for such thieving of production in this case by the fact that the closed in pressure dropped over 150 lb./sq. in. in a period of one month.

With regard to Well "C," the question as to whether production is lost or deferred depends on the ultimate rate of decline. If this is appreciably flatter than the curve of a normally-produced well, the production is deferred. By the comparison of average decline curves plotted on a logarithmic plat with those of individual wells some idea should be gained as to whether the area between the potential peaks will be regained subsequently.

With regard to the statement that with wells closed in there is rapid expansion of the gas cap, it certainly seems strange that by increasing the reservoir pressure the gas cap should be increased. One would expect the exact converse to be the case. If there is an increase it is more likely attributable to :—

(*a*) Increased production of neighbouring wells as a result of the shut down.

(*b*) Thieving of production into a lower pressure sand where differentials of pressure exist.

He had found that where interference is suspected, the closing in of one well will increase the production of the neighbouring well. Such effects vary greatly in character. Thus, many wells to the same sand, spaced at 300-foot centres, do not show this effect, yet in one instance it was suspected over a distance of approximately 600 ft. In this case the wells were both flowing and making some water with the oil. One well ceased to flow, and owing to heaving sand conditions flow could not be reinduced. The other increased in production by about 100 brls. per day, and at the same time there was a marked diminution in the water content. The period elapsing between the shut down of one well and the increased yield of the other was over a month. Although it is possible that this increase was natural, it should be pointed out that the well in question had been producing for over two years with marked constancy, both in the oil and water yields.

Recently he had observed a similar phenomenon in pumping wells, where one well increased its yield almost 50 per cent. as the result of the shut down of a neighbour.

In Trinidad many of the producing sands are lenticular in character, and by virtue of their non-persistent nature there is

not the danger of excessive thieving. Some sands do persist, however, and in these any restriction should be applied to all wells in the vicinity.

Although, fortunately, there had been no necessity to adopt a drastic restriction policy, he thought the following should be guiding principles in Trinidad :—

(a) The avoidance of shutting down oil/water producers. A head of water on a producing sand may aid water travel.
(b) Careful observation of casing-head pressures on all shut down and excessively restricted wells. Abnormal falls in shut in pressures or rates of decline greater than normal point to thieving.
(c) The coring of producing zones. This must aid to a conception of the persistence or non-persistence of sands and will aid in the selection of wells to be shut down.
(d) The avoidance of exposing various distinct producing zones by one string of perforated. In such cases differentials of pressure are liable to occur and will aid thieving.
(e) Aim at the most economical gas/oil ratio for the production deemed necessary. Thus, if there is a marked decrease in efficiency in one well as a result of restriction, try restriction at another of roughly equivalent yield.

Mr. J. M. Penny said that his views on the subject were similar to those already expressed by the Chairman. Referring to the statement by Mr. Elias that :—

> "I understand that production engineers have found that wells high up on the structure and with big gas/oil ratios come back very badly after being closed in, and I understand that there are cases of such wells in Moreni which yielded only gas after being closed in for periods."

In his opinion that statement pointed to the fact that a possible explanation of that phenomenon was that a barrier was set up in the producing sands surrounding the wells, due to what might be the occurrence of a Jamin effect aggravated by the closing in of the wells. It had been experimentally proved to what a marked degree the free porosity of a sand might be reduced by the resistance of gas-bubbles to distortion in passing through the sand pores, and also the extent to which the surface tension of the oil stored in the sand might be increased owing to the lighter fractions having had an opportunity of escaping.

Mr. C. E. Capito said it seemed a pity that more than half of the decline curves had not been printed.

With regard to well " B " the decline curve seemed to him to show a substantial increase in production instead of a slight

decrease. The top peak in March showed nearly 40 per cent. more production than in July. It would be interesting to know what were the peculiar conditions existing in Rumania to which Mr. Elias referred. The decrease in casing-head pressure would appear to indicate a rising fluid level in the well, which would seem a normal procedure when the well was closed in.

There is no mention of the amount of sand produced by any of these wells. The quantity of sand produced would have a considerable bearing on the decline curves, as the bottom oil perforations might easily be closed up by the roof having fallen, leaving only room at the top for the gas and a small quantity of the oil to come in, raising thereby the gas/oil ratio.

No mention is made in the discussion as to where the bottom of the tubing is, or whether they use tapered tubing or not. If the statement that the loss of oil is due to drainage down the structure is correct, it seemed to him that such wells should be closed in, in any case, to prevent loss of gas. This would appear to be the correct procedure, whether the well was restricted or otherwise and the decline curve, if the well had been continuously produced, should surely have shown this effect. Do the wells lower down the structure show the increase of production which has been lost by wells up the structure ? It would be interesting to know if they have ever tried pulling or side-tracking their oil-strings and replacing with new oil-strings to endeavour to get back production.

If thief sands were responsible they would surely give back their oil as the production of the well declined.

He was wondering how many people would agree with the statement that decrease in bean size means decrease in ultimate production and rapid expansion of the gas cap.

Turning to Trinidad, for some time past he had been examining records to see what did happen to the production of wells that were closed in for any purpose.

There would appear to be four types of wells here :—

1. Those that come in with a very large initial production and then never do anything afterwards.
2. Those that come in with a more reasonable production and decline very quickly and then die out.
3. Those that come in with a similar more reasonable production and keep up a steadily declining production and then suddenly cease to produce ; and
4. Those that come in with a reasonable production and have produced or are producing at a steadily declining rate.

There are a certain number of wells that do not fall exactly in any of these categories, such as those that have periods of rejuvenation, etc., but he thought the four types take into account the majority of the wells in the Island.

With the exception of one area there are very few wells that have been closed in and re-started without deepening.

Until comparatively recently the majority of wells that can produce have been produced steadily from the start until they have either ceased of their own accord, have now been closed in, or are still producing. In fact, wells closed in and re-started have really been confined to three areas in this Island, in only one of which has any large number of wells been shut in.

In this area, of about 40 or more wells closed in 16 have shown increased production, 2 have continued on the same decline curve, and 8 have shown decreases in production. The remainder have either not been started up or have not been started up sufficiently long to be able to give any indication of what is going to happen.

The majority of cases where an oilstring has been withdrawn or side-tracked and replaced by a new oilstring show a successful effect on the production of the well. From this it would appear that when a well ceases production, it does not necessarily mean that it has abstracted all the oil in its neighbourhood, and it would seem evident that the perforations or screen have become clogged with mud, clay or sand, which prevents access of oil to the well. This seems very noticeable in certain wells, which have a very sharp decline as the gas/oil ratio appears to increase to a very large extent.

Turning to America, a paper by Mr. L. G. E. Bignell[4] shows that the Prairie Oil Co., by shutting down on Sundays, has done so with practically no loss of production. In fact he says on sixteen leases there has been a marked increase in production; and in others, after a drop of 9 per cent. in production, the wells have gradually come back on to the projected decline line on the production curve. He further states: "There seems to be numerous cases where production has actually benefited by shutting down the property for a time. When opened up many wells have shown a decided increase in production, not only at the time of re-opening but for a very considerable time after, though data are not available to determine what the ultimate effect will be." This good effect, however, does not seem to be general in America, as he states that "in California some wells were benefited while others were injured by being shut down."

[4] *Oil & Gas J.*, 25.6.31.

C. L. Moore[5] states, with regard to the effect of shutting in wells :—

"As a rule very little, if any, loss in ultimate recovery was indicated, based primarily on a study of decline curves before and after the shut in period."

It would, therefore, appear that restriction is, on the whole, by no means injurious, but care should be taken with the methods employed in closing in or restricting wells and large jumps in bean size should be avoided.

Mr. W. Van Achterbergh said that from the statistical data furnished by Mr. Capito it came out very clearly that shutting in of wells produced a rather different effect for various wells. One may therefore ask what is actually happening when a well is shut in ?

If a well has been producing from a certain sand for some time, a depletion area is formed around this well breaking the formerly existing equilibrium in the sand from which it has been producing. Oil is pushed into this area of depletion by the gas pressure prevalent in the non-affected parts of the oil sand. When the well is shut in its area of depletion is gradually repressured and refilled with oil, due to the existing excess rock pressure in the non-depleted portions of the oil sand, which themselves consequently suffer a slight drop in pressure. If restriction lasts long enough an equalisation of pressure throughout the sand must result.

Bearing this in mind, it should not be astonishing at all that by opening up a well after restriction an increased production as compared with the last production before shutting in will result.

On the other hand, a smaller production must be expected in wells to be drilled in to the undrained parts of the oil sand which supplied the extra pressure for refilling the different depletion areas in the same oil sand.

In discussing the effect of restriction on production it may, therefore, be maintained that taking one well into consideration leads to wrong conclusions.

The question should be asked whether the ultimate recovery from the oil sand changes when wells are being shut in. The speaker doubts whether this is the case.

It is not to be denied that after opening up some wells yield a worse production than before. This is exclusively to be attributed to mechanical difficulties, such as sanding up and filling up of draining channels, due to a sudden breaking of the existing equilibrium. In this respect it may be emphasized that beaning up is always a dangerous thing to do.

[5] *Intern. Petr. Techn.*, Sept., 1931.

Mr. L. A. Toone said that it struck him that there had been no distinction made between restricting a well by beaning it back and by shutting it in altogether. Though it may in some respects not make much difference, it certainly made a difference to the theory referred to by the Chairman that shutting in a well altogether produces some capillary effect in the oil sand which causes a diminution in production from the well when it is again opened up. In the case of beaning, where the flow towards the well was only reduced instead of being stopped entirely, one would not get the same effect.

Personally he had had very little experience with restriction of production by alteration of beans, but on one field restriction was carried out by closing in altogether a number of wells, and it was found there, when first experimenting, that if wells were shut in here and there on account of their being difficult producers, etc., differing results were obtained. These, however, usually, showed that production lost from one well was not entirely lost but went to another well instead, although there were certainly cases where oil was lost by flooding. Later on, the field being naturally divided up by faults into a number of natural blocks, wells in a block, perhaps 30 or 40, were shut in altogether. On opening up later, in this case there was found to be no serious increase of water in the wells and little change in the oil production.

Mr. A. J. Ruthven Murray said that he would like to mention one or two points appertaining to the behaviour of restricted wells.

One was, that he had had experience of producting oil from wells in which oil sands were interbedded with water sands ; the production from which was obtained by passing the mixed fluid through an oil/water separator kept at tubing pressure. In these wells, due in all probability to the pressure of the water sands being lower than that of the oil sands, they found that the more they beaned the well down the greater was the percentage increase of oil over that of water.

He quoted an interesting statement from a petroleum technologist in Venezuela to the effect that in 1927, when there was a minor depression, several wells were closed in for a period of seven to eight months. These closed-in wells were up flank on a regular structure, those allowed to produce were two to three lines of wells down flank and offsetting the wells of neighbouring companies. When these closed-in wells were opened up a large percentage of them would not flow and, moreover, could not be induced to flow. It was then found that bottom water which had never previously been suspected had encroached around these wells. Consistent swabbing failed to bring in oil, only a small volume of salt water. These wells were tested with a

"water witch" and the bottom of the holes plugged off, after which some of them produced oil at a considerably reduced rate, but most of them had to be abandoned. The other wells down flank which were allowed to produce all the time were not affected.

This paper is entitled: "A Discussion on the Behaviour of Restricted Wells"; it has been most interesting, but it clearly points to restriction of drilling as being the best method of restricting production, and, second to that, the importance of a structure being under the control of one or at the most two companies and not divided up into small areas under the control of many owners, such as is the case with town lot holders in California and as mentioned by Mr. Millar, also exists in Rumania.

Mr. H. D. Fletcher said his experience of closed in wells had been that when they were opened up they gave increased output for a short time and then dropped back to their normal rate of decline existing at the time they were closed in.

If they did not come back he generally resorted to cleaning out or swabbing.

The pressures mentioned by Mr. Elias were high, so that bailing or swabbing would have to be done under pressure conditions.

There was no mention as to whether the wells made sand or shale, or whether the perforations got choked, and this should be investigated before accepting the theory that the production was being lost in denuded sands.

When a well is closed in a very small accumulation of sand or shale will often shut it off or greatly reduce its output, and swabbing or jetting the perforations will often bring it back.

If the decline continued at the same rate when the well was shut in as when open, there must have been a continuous loss all the time the well was producing, that is if denuded sands were exposed.

It is phenomenal that the wells should show the same decline when shut in as when open.

The question as to whether the production was lost or only deferred could only be investigated by mechanical means such as applying pressure to sections of the sands, isolated by packers, and so ascertain if denuded sands were exposed; if they were not, and the well held pressure greater than that recorded by its own gas, then there must be some other cause, such as clogging of the perforations or closing up of the flow channels through the sands to the well.

After exhausting all recognised methods of bringing the well back, and without success, he did not see how you could arrive at a decision other than that it was the well's normal rate of decline.

One of three things appears to be certain, either the flow channels to the well were restricted or closed up, in which case the gas

pressure should drop, denuded sands were absorbing oil and gas at the pressures recorded or the drop in output was the well's normal decline.

Mr. J. L. Harris said the point which the first reading of the paper brought home to him was the necessity of standardizing weights and measures.

In the first place, he would like to define restriction. The definition he submitted was the curtailment of production of a well below its maximum economic rate. Some wells have been or are being produced to give the last drop of oil, but that procedure was not necessarily economical, That is to say, if you pumped a well for eight hours and aggregated 90 per cent. of the production which you would obtain in 24 hours, it was not economy in the great majority of cases to produce the well by the pump for 24 hours. On the other hand, he would definitely deny that pumping such a well for 8 hours was a form of restriction, hence the definition.

In the case of uniform underground conditions with rigid definitions between water and oil sands, there appears little reason to doubt that no loss would occur. If time was of no value and casing everlasting, the mean economic rate in such desirable circumstances would be the rate at which the lowest gas/oil ratio was obtained. Any deviation from this rate would decrease oil recovery, and so if restricting the production increased the gas/oil ratio, some loss would probably result. Unfortunately nature has not arranged conditions in such a very desirable manner in Trinidad, and this being so he thought that nothing short of experimenting on individual wells could determine what effect restriction was likely to have. The only definite effect that he had observed with restriction was that in one class of wells it definitely decreased production. Generally he was of the opinion that there was an economic rate at which a well might be produced. Any deviation from that rate would lead to loss of profit. The economical rate may be affected from time to time by artificial factors, such as neighbouring producers, the price of oil, mechanical hazards, etc. Theoretically, wells should be produced to give the maximum ultimate production or the maximum percentage of recovery. It did not necessarily follow that maximum profits accrued from such a policy, though in general it was a reasonable approximation to the optimum method of production.

A policy of operation which tended towards the maximum ultimate recovery was probably the economic criterion, but in abnormal conditions as at present, with the uncertain wide variations in the price of oil which made it impossible to forecast future values of products might make a policy of restriction pay even if such a policy led to a loss of ultimate production.

He noticed that a member was exercised as to where the lost oil went and suggested thief sands. It was quite possible that thief sands may absorb some of the production, but most of it might remain in the sand and not be produced, probably due to the collapse of drainage channels and loss of gas.

Restriction of normal production below a certain point probably entails loss of ultimate production, especially if the restriction was for a lengthy period.

It could not be too definitely stated that there was no similarity in production of oil from a Trinidad oilfield and the taking of oil from a storage tank. But economic results were impossible if more oil was required from a limited number of producers at one period and less oil at another period. There was an economic rate which could not be deviated from without severe increase of production costs and probable loss of ultimate recovery.

Col. H. C. B. Hickling said that he could not agree with Mr. Harris. Profit was the thing aimed at, and although in many cases the maximum ultimate recovery might give the greatest profit it was not the same thing, because although one might be able to obtain by a certain method the maximum ultimate production from a field, it was useless if it could only be sold at a loss. It might be that the maximum profit could be obtained when producing less than the maximum ultimate recovery.

On the motion of the Chairman a vote of thanks was accorded to Mr. Capito for reading the paper, and to their hosts the President and members of the Apex Club for the use of the building.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE TWENTY-NINTH GENERAL MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held on April 27th, 1932. The following paper was read :—

A Note on Mud Flow.

By C. C. WILSON (Associate Member).

In a previous short paper[1] the writer introduced the subject of Green Clay Mud Flow, with reference to that found in the Forest Clay section in wells and exposures at Palo Seco. In that paper the view was emphasised that this remarkable fossil flow occurs as a sheet intrusion, or better, a sheet injection. It is still considered that injection is the true explanation and that ejection, meaning outbursts of mud on the sea bottom during Forest Clay deposition, similar in nature to the volcano islands off Chatham of 1911, and 1928, is far less probable.

The flow consists of St. Croix pebbles, principally fragments of brown, marly clay, up to 1½ in. in diameter and carrying abundant Globigerina and a typical St. Croix assemblage, also small black and white chert pebbles characteristic of the Herrera conglomerate set in an unstratified green grey silty clay matrix. The pebbles invariably show highly polished or slickensided surfaces suggesting considerable squeezing and rubbing against one another. Often the pebbles are wetted with oil on their surfaces, and pebbles of sandstone are oil-stained throughout.

The flow is generally associated with highly slickensided zones within the Forest Clay. In the Canari district (between Canari Bay and the Guayaguayare oilfield) a flow identical with that at Palo Seco has been found, again within the Forest Clay.

Green Clay Mud Flow at Palo Seco occurs between 0 and 100 ft. above the base of the Forest Clay and varies between 1 and 40 ft. in thickness, sometimes divided into several layers, and the area now known to carry this flow is about a mile broad by two miles long. It is difficult, owing to irregularities in the base of the Forest Clay itself, to determine whether the base marks a stratigraphical plane, but it is possible that the base of the Mud Flow forms an even better marker than the clay and actually represents

[1] *J. Inst. Petr. Techn.*, 1930, **16**, 578–580.

a true time plane. The fact that only the Forest Clay carries this particular flow, and that the base of the flow marks approximately a stratigraphic plane, does suggest that during Forest Clay deposition an outburst, or series of contemporary outbursts, of mud as submarine mud-volcanoes resulted in the formation of cones of Green Clay Mud Flow which were subsequently redistributed in sheets by marine currents.

It seems impossible, though, that the flow should have maintained its individuality and homogeneous structure under such conditions of deposition. One would expect to see a certain stratification and some admixture of Cyclammina Clay detritus and fauna, but one does not. The Mud Flow is identical in characteristics throughout, its only variation being in thickness (maximum 40 ft., minimum 1 ft.), and sometimes even occurs in separate stringers.

It is unfortunate in Palo Seco that coring has been restricted mainly to the zone of the base of the Forest Clay, otherwise it is possible that further flows and, perhaps, necks and dykes in similar incompetent clays might have made their appearance. Actually, the chance of hitting a neck in a cored well will be less than 1 : 10,000. The horizontal flow itself was not found until 53 wells had been drilled; since then 20 well-sections have shown Mud Flow.

In the Palo Seco neighbourhood it has been proved by drilling that more than 3500 ft. of Naparima sediments intervene between the St. Croix series and the Forest Clay with its injected flow.

At the time of deposition of the Forest Clay the beds, 3500 ft. or more in thickness, were lying horizontally above the St. Croix and had not yet been effected by the late Tertiary mountain-building movement. It appears incredible that oil and gas occurred in concentrations of sufficient size to lift large bodies of Mud Flow 3500 ft. vertically through undistributed strata.

It seems far more feasible that during Moruga and later deposition, when the orogenic movement came into operation, stresses were set up, causing folding with areas of compression on structural flanks and areas of tension along a plane of movement, lubricated by salt water, gas and oil, moved in the form of mud to areas of low pressure and became intrusive into overlaying incompetent formations. It is suggested that if mud can migrate vertically, whether by injection or ejection, to such an extent, how much more easily will oil and gas (and salt water) travel under tectonic stress. In the previous paper it was mentioned that, underlying the area of Mud Flow, high-grade oil (29° to 35° Bé.) was found, whereas in other areas, separated from Mud Flow, oil of

22° to 29° Bé. was the rule. Is it not possible, therefore, that Oligocene Marls and Lower Green Clay rather than Cyclammina Clay (Naparima) form the mother rock of Trinidad oil, and that areas carrying light oil accompanied by Green Clay Mud Flow in the Cyclammina Clay indicate areas of migration from the Oligocene? Areas of heavy oil in Palo Seco occur as fringes to the main accumulation, and have possibly been influenced by their contact with connate water during movement under pressure within the Naparimas (as suggested by Emmons, Geology of Petroleum, p. 41).

On this assumption, and assuming that accumulations in the Oligocene were controlled by structure, migration must have impregnated beds overlying crestal zones or high-flank zones in the Oligocene.

An extraordinary parallel to Green Clay Mud Flow is seen, in Ecuador, in the formation known as "the Clay-Pebble Bed" which occurs between about 1000 ft. to 2500 ft. below the top of the Eocene. The top of this formation marks approximately the top of oil accumulation. In physical characteristics, this formation is identical with Green Clay Mud Flow even to the point of carrying black and white chert pebbles, but, unfortunately no striking difference between the fauna contained in the pebbles and that of the surrounding beds is visible. Extensive cliff exposures show that this formation has no relation whatsoever with bedding, but has every semblance of injection. Here, again, the oil is of high grade (40° to 50° Bé.). In Peru, the main production is obtained from lower Eocene beds; in Ecuador production is obtained, so far, only from beds above the middle of the Eocene. It is just possible that the Clay-Pebble Bed, acting in the same manner as Green Clay Mud Flow, has accompanied the migration of oil into higher strata.

The writer is of the opinion, therefore, that in large areas of Southern Trinidad, deep drilling will show that existing producing horizons do not represent the main body of accumulation, but that the extensive visible distribution of oil (Eocene to Pliocene) is merely the result of large scale migration from lower major accumulations, controlled by structure, invisible at the surface and entirely independent of the Miocene folding.

DISCUSSION.

Mr. P. W. Jarvis said that he thought the author was getting on to the right track. Whereas geologists in Trinidad used to think that the local oil originated in the Cruse beds directly underlying the Forest Clay (Miocene), and that no great upward migration

of oil from the mother rock had occurred, Mr. Wilson now suggested that the oil appeared to be an upward migration from older beds (Oligocene).

He asked, therefore, whether it was not possible that the migration was from still older beds in the series, from the Cretaceous. There was a growing idea in the United States that the Cretaceous beds were the original source of the oil found in Trinidad, Venezuela, Mexico and the coastal plains of the United States, and that these countries jointly formed one field. This idea might not be correct, but it would be well to bear it in mind.

While his remarks did not touch on Mud Flow, the subject of the paper, he felt sure that in writing the paper the author was also thinking of oil.

Mr. G. A. Richards said he had seen specimens of these Clay-Pebble Beds, Mud Flows or clay conglomerates in Trinidad, and he had also seen outcrops in Peru and hand specimens from Ecuador. Other observers who had examined the outcrops in both Ecuador and Peru stated that the two were identical; the material from Trinidad appeared very similar.

In Peru he thought it was first discovered in 1926 in a small area. As work went on it was found over wider and wider areas, and it was believed that some of the deeper wells in the main field had actually penetrated this bed. As the cable tool system was employed there and no cores were taken, it was impossible to be certain, but judging from the appearance of bit samples, it would appear that bands of Clay-Pebble Bed material had been penetrated in some wells. If this was actually the case, production was obtained in that field both from above and below the Clay-Pebble Bed.

He personally inclined to the view that this material was not simply Mud Flow. The angular form and highly polished surfaces of the Clay Pebbles, as well as the highly polished chert pebbles, included in the matrix, suggested that such polishing had been achieved by motion under very high pressure, and he was inclined to believe that these beds were a type of fault breccia, as originally suggested in a paper by Barrington Brown and Baldry.[2]

He had seen one exposure of it in Peru where there was a conical hill, named Cerro Organos, on the sea coast. The top of this hill was formed of undisturbed stratified rocks, clays and sandstones, and underneath that capping of undisturbed rock there was a mass of thoroughly broken up formation including large masses of Clay-Pebble Beds. The broken up beds consisted of

[2] *Q.J.G.S.*, 1925, **81**, 454–460.

rocks of different ages and lumps of practically all sizes lying at all angles in a matrix of clay. The whole of the matrix was not a Clay-Pebble Bed, but " seams " of Pebble Bed occurred throughout this broken zone.

Mr. J. L. Harris said that he was inclined to regret that the author had reopened the idea of Cretaceous oil in Trinidad. He had hoped that this perfectly sound theoretical proposition had been side-tracked for the present, as practical results gave no indications of the presence of commercial deep-seated oil.

He was firmly of opinion that all the oil in Trinidad that had been exploited commercially so far was certainly migratory, but it did not follow that migration necessarily indicated presence of oil in the mother reservoir.

Mr. G. H. Scott said he noticed that the author stated that the Mud Flow seemed to afford a better stratigraphical marker than the base of the Forest Clay, and further that there were no signs of redeposition, but that the Mud Flow appeared to be injected.

These two statements are difficult to reconcile. An injectional phase might in some instances parallel the dip when it travels along bedding planes, but was far more liable to follow cracks and crevices which might lie at any angle to the dip. The fact that the Mud Flow appeared to be a reliable marker for the structure argued strongly for redeposition.

The author cited a variation in the oils as being extraordinary. Such variations in oils occurred in Trinidad, where there were no signs of faulting, fissuring or injection. In the Fyzabad structure wells only 600 ft. apart yielded oils of a gravity of 0·9023 and 0·9652 from the same sand, and the location of the marker bed showed there was no tectonic disturbance between the two.

The author cited the possibility of injected oil sands. These undoubtedly existed in the Apex field, and it was hoped that the matter would form the nucleus of a paper at a later date. These injected oil sands varied from mere stringers, which had been traced over 40 ft. in cores, to oil sand dykes of several feet in thickness. Their injectional character was proved by the sub-angular fragments of clay torn from the country rock which were found along the margins of these dykes.

In the course of the discussion it had been said that the paraffin base oils and the naphthenic base oils were of different age. He could not agree with this as a general statement, although it might be true in certain instances. In the St. Croix beds exposed in the

Moruga district there were type asphalt and ozokerite deposits in one and the same sand outcrop separated by a lateral distance of about 2½ miles.

With regard to the lithological characteristics of the Mud Flow, he considered that while in certain cases injection seemed to have been proved, the possibility of redeposition could not be ruled out altogether. A bed in many ways analogous to that described was found at the base of the Green Clays in the Rio Claro district. It had a Green Clay matrix with sub-angular pebbles of marl and very small chert grains. In this case there was no possibility of injection, and this bed was a passage bed between the underlying marl mass and the Green Clays.

The Author, in reply, said that he was interested to hear Mr. Jarvis' views on the possibility of oil being derived from the Cretaceous, as in Mexico and certain areas in the United States.

In reply to Mr. Murray, he wished to say that the author's remarks comparing the occurrence of Mud Flow in Trinidad and Clay-Pebble formation in Ecuador were based on observations in the field on the Ancon Cliffs of Ecuador, where no definite thrust feature was evident.

The exposed Clay-Pebble Bed was entirely irregular, occurring both parallel to dip and also sometimes at considerable angles with the dip, breaking abruptly across the stratification without warning and at the same time showing extreme irregularity in thickness.

The evidence from drilling shows that the Clay-Pebble Bed was found throughout 3000 ft. of beds in the Upper Eocene.

The view held by some observers that Scree detritus from the Andes or from foothills, falling into the sea, appeared to be contradicted by the fact that between Clay-Pebble occurrences the Eocene clays (Socorro) shows well stratified undisturbed and uncontaminated deposits. Further, a continual supply of Scree detritus during the deposition of 3000 ft. of beds would necessitate a very mixed accumulation of rocks. In fact, it is thought that the Clay-Pebbles themselves are similar in age to the surrounding formation. The grit and pebbly sands associated with the Clay-Pebble Bed might be derived in a similar manner to the gritty clays of the St. Croix (basal Miocene) of Trinidad.

The Author had not had the opportunity of seeing the exposures of Clay-Pebble formations to which Mr. Richards referred, and he, therefore, could not give an opinion as to the nature of its occurrence, but he suspected that it was intimately related to the formations of the Clay-Pebble Bed at Ancon.

Regarding Mr. Harris' acceptance of the migration of oil upwards, but that possibly no reservoir rock exists in lower beds, it was very evident that cliff exposures both at Erin and Palo Seco Beach showed abundantly large saturated sand bodies belonging most certainly to the older beds (Oligocene).

It was not known, however, whether these sands extended to any distance to the north.

Mr. G. H. Scott had quoted gravities of oil at 0·9023 and 0·9652 in wells at 600 ft. apart. It might again be suggested, as at Palo Seco, that this increase in gravity indicated the approach of the petroliferous horizons to water zones in which the oil, migrating under pressure, had forced connate water away from the original point of migration and became somewhat altered by salts in the water during its progress.

On the motion of the Chairman a vote of thanks was accorded to the Author for his paper.

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